

(19)日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開2001-220527

(P2001-220527A)

(43)公開日 平成13年8月14日 (2001.8.14)

(51)Int.Cl.⁷

C 09 D 11/00

識別記号

F I

C 09 D 11/00

テ-マコト⁸(参考)

4 J 0 3 9

審査請求 未請求 請求項の数2 O L (全 8 頁)

(21)出願番号 特願2000-33305(P2000-33305)

(22)出願日 平成12年2月10日 (2000.2.10)

(71)出願人 591075467

富士色素株式会社

兵庫県川西市小花2丁目23-2

(72)発明者 小西 秀樹

兵庫県川西市小花2丁目23番2号富士色素
株式会社内

(72)発明者 鈴木 尚

兵庫県川西市小花2丁目23番2号富士色素
株式会社内

Fターム(参考) 4J039 AB02 AD07 AD09 AD10 AE06

AE07 AE11 AF07 BA04 BC12

BC13 BE01 BE12 BE22 CA07

EA10 EA19 EA42 EA44 EA47

FA05 GA24

(54)【発明の名称】 インクジェットプリンタ用溶剤系黒色顔料インク

(57)【要約】

【目的】カーボンブラック顔料を用い、浸透性材料に高速で精細なインクジェットプリントが可能なインク組成を開発することが本発明の目的である。

【構成】着色剤と有機分散媒体および分散剤を必須成分とするインクジェットプリント用溶剤系黒色顔料インクにおいて、着色剤に特定の顔料を、分散媒体に特定のグリコールエーテルを、分散剤にこれらに有効な樹脂系化合物を用いることで、顔料が微細粒子として分散してプリンタ内部の細隙通路を順調に通過し、かつ長期の放置や保管において粒子が凝集しない、ならびに印刷後に媒体がすみやかに浸透性材料内に浸透してインクが滲むことなく固化するインク組成を見出して目的を達成することができた。

【特許請求の範囲】

【請求項1】 顔料と有機分散媒体および分散剤を必須成分とするインクジェットプリンタ用溶剤系黒色顔料インクにおいて、顔料としてD B P吸油量が15以上180(m1/100g)以下であり、pHが2.0以上4.5以下の範囲内の酸性を呈するカーボンブラックを、顔料の分散媒体としてエチレンオキサイド鎖またはプロピレンオキサイド鎖の重合度が2以上4以下のポリエチレングリコールのモノブチルエーテルまたはポリプロピレングリコールのモノブチルエーテルからなる群から選ばれた1種、あるいはそれらの2種以上の混合物を、分散剤として上記着色剤と分散媒の組合せに有効な樹脂系化合物を用いること、および顔料粒子の98.0wt%以上が粒径0.01μm以上1.0μm以下であって、平均粒径が0.02μm以上0.5μm以下の範囲内にあって安定に分散していることを特徴とするインクジェットプリンタ用溶剤系黒色顔料インク。

【請求項2】 インクの必須成分100重量部あたり、顔料が1.0重量部以上15.0重量部以下、分散剤が使用する顔料の0.1重量倍以上2.0重量倍以下、残余が分散媒である請求項1に記載のインクジェットプリンタ用溶剤系黒色顔料インク。

【発明の詳細な説明】

【0001】

【発明が属する技術分野】 本発明は紙や木材等の浸透性材料面にインクジェットプリンタで印刷する際の溶剤系顔料インクに関するものである。

【0002】

【従来の技術】 近年インクジェットプリント方式の印刷技術が開発され広く一般に利用されはじめた。種々の方式が提案され実用化段階に到っているが、それらに共通するのは微細なインク液滴を形成しつつ高速で噴射して対象面にインクで像を作ることである。インクの着色剤として染料は、各種媒体に溶解させうるので、均一な溶解状態でのインクとして微細な液滴を形成しつつ噴射するのに適している。しかし、染料は耐光性や耐水性に難点があり使用の局面に制約がある。一方、顔料は耐光性や耐水性に優れているので好ましいが、それを溶解する媒体がないため微細粒子の分散液として使用せざるをえない。印刷精度の要求からプリンタヘッドのノズルやノズルに到るインクの供給路は微細であり、そこを通過する顔料の粒子径はさらに微細であることと、使用時や保管時に凝集したり沈降したりしてはならない、すなわち、微細な分散状態が安定に保たれることが顔料インクにとっての必須条件である。顔料インクはいくつかの分野で実用に供されているが、インクジェットプリンタの過酷な条件に耐えるような、顔料の安定な微細分散が難しいため当該分野での顔料インクは未だ実用化されていない。他の印刷法と同様、より耐久性の、より精細な、より高速あるいはより大面積の印刷が求められる以上、

インクジェットプリントにおけるインクへの要求はより厳しくなる宿命にある。

【0003】 そのような背景でインクジェットプリンタ用の顔料インクが望まれるのであるが、顔料の耐光性や耐水性は問題なく良好なもの、水系分散ではインクの乾燥あるいは固化速度が遅いため印刷直後の印刷像が接触によって乱れたり、分散のための工夫があだになって印刷物の耐水性が劣る場合が多くあるので、非水系での顔料分散が好ましい。また非水系分散媒のうち、揮発性溶剤は印刷後溶剤の蒸発による速やかなインクの乾燥固化が期待できるが、印刷時等取扱い時に揮発による組成の変化が起こりやすく不適当である。比較的難揮発性の溶剤で、印刷時に、紙や木質の浸透性対象面の内部に速やかに浸透してインクが固化するならば、顔料が対象面表面で拡散したりあるいは接触により印刷像が滲んだり乱れたりすることがなく、精細な印刷が可能と想定される。このことはプリントヘッドの微細部分にインクが良く浸透して確実にインクが供給できるかということと同種の問題のようである。しかし、どのような分散媒が顔料や分散剤との関わりにおいて、安定な微細分散とこのような良好な浸透流動性を兼備し、より高速の印刷に対応できるかとの知見は皆無のようである。

【0004】

【発明が解決しようとする課題】 顔料の微細な安定分散とインクの浸透流動性をともに確保する、非水系の分散媒に顔料を微細分散したインクジェットプリンタ用顔料インクの開発。

【0005】

【課題を解決するための手段】 新規のインク組成や配合比の選択により目的達成を期する。

【0006】 非水系の分散媒に顔料を微細分散したインクジェットプリンタ用顔料インクの開発を目指す場合、対象として最適のインクジェットプリント方式はインクの微細液滴化と噴射をピエゾ素子で行うピエゾ方式であるので、その方式を例にして本発明の内容をより詳細に述べることにする。ピエゾ方式では電気振動を力学振動に変換してインクに伝え、インクをノズルの微細な複数の孔から対象面に向けて微細液滴として噴射する。微細液滴の噴射はピエゾ素子への電気振動入力により制御し、対象面またはプリンタノズルの移動で対象面上のインクの到達位置を制御して所望の像を描くのである。ノズルの孔の開口径は通常数十μm、そこに到るインクの供給路の径は通常数十μm以上数百μm程度であり、その中間で通常数個の孔の開口部を望む位置にピエゾ素子が配置され、ノズル全体では通常数個から数十個の素子が配置されている。開口部やその近辺の流路が微細であるから、当然顔料の安定な微細分散が必須条件になるのである。

【0007】 インクジェットプリンタ用以外の顔料インクで、顔料と分散媒および分散剤をどんな組合せにすれ

ばよいのかという単純な問題であれば、ある程度の推測は可能であり、現に加熱あるいは熱サイクル下に保存した時顔料の微細な分散状態やインクの粘度に変化がなく安定と見なされるインクを調製したが、印刷試験開始当初順調に印刷できたインクが、暫くするとインクの噴射が停止するのである。すなわち、従来各種インクの開発において採られてきた尺度が役に立たないのである。本発明者らの他の検討によると、例えば水と相溶性のある親水性の高い溶剤を分散媒とすると、分散剤の工夫でインクの噴射の継続性はある程度向上するものの実用的な印刷速度で長時間の印刷ができないし、疎水性の強い溶剤を分散媒とすると分散剤を種々工夫してもインクの噴射は前述同様不適当であった。すなわち親水性あるいは疎水性という単一の尺度や分散剤という単一の尺度では、解決の目途がたたないのである。インクが印刷時のピエゾ素子の例えば数千Hzという高速振動にも耐えて微細な流路を安定に通過しうるか、また以下に述べるような諸要求をも同時に満たせるかというと、従来公知の知見では解決の指針がえられない。

【0008】噴射により減量したインクは、供給路他端のインク溜めから細管である供給路での毛管現象で補給される。ノズル先端へのインクの補給をスムースに行うにはインクの表面張力や粘度特性を選ばねばならない。表面張力が大きいほど毛管現象には一般的には有利であるが、インクを最初に充填するとき等に流路に気泡が発生したり残りやすく、それが印刷中に流路を閉塞することが考えられる。凝集顔料によるか気泡によるかを問わず、いったん閉塞するともはやそのノズルはインクの噴射が不可能になるので、印刷を中止してインクの流路を洗浄し直さねば使用できない。溶剤単独でも噴射停止の起こる場合が多く、超音波振動で予め脱泡したり、インクの分散剤として界面活性剤を検討したがいずれも改善できなかった。インクの粘度は高すぎると流動速度が遅く、高速で行われる噴射に対応する細管中の高速流動が不可能でインクの供給が追従できないし、低すぎるとノズルから溢流して印刷像がインク過剰で乱れる。また粘度の絶対値の議論以前に粘性挙動がニュートン流動でなければ不都合が生じる。表面張力や粘度特性は噴射されたインクの細滴化にも影響し、印刷像からみて適正な大きさの液滴を形成するのに適した範囲がありそうである。しかし、具体的には不明である。

【0009】噴射されたインクの複数液滴は対象面上にサブミリメートルからセンチメートルときにはそれ以上の線幅の印刷像を形成する。線幅やその断続長はピエゾ素子の作動により制御される。印刷の対象面は紙や木質の浸透性面であるので、分散媒は顔料を表面に残して面内部に速やかに浸透し、顔料が対象面の表面で拡散したりあるいは接触により印刷像が滲んだりすることのないような物質である必要がある。このことはプリントヘッドの微細部分にインクが良く浸透して確実にインクが供

給できるかということと同種の問題であるが、ヘッドが金属製であるのに対し、印刷対象面はセルロースやその他の天然あるいは合成の有機高分子や無機の充填物質を含有して構成されているので同一には論じられない。

【0010】以上のように多岐にわたる諸要求を同時に満たす組成配合の手がかりは、容易には得られないものである。本発明者は多くの試行錯誤の結果、有機分散媒体としてオレイルアルコールを選ぶと、種々の顔料を用いてインクジェットプリンタ用溶剤系顔料インクを構成できることを見いだし、すでに特願平11-209022として出願した。しかし、その後の検討によると既出願のインクは分散安定性や印刷特性に優れるものの、実用上はさらに高度の分散安定性を具備すべきであることが判明した。このため本発明者らは改良研究を続け、黒色インクに関する本発明に到達した。

【0011】本発明のインク組成において、着色剤である顔料はD B P吸油量が15以上180 (ml/100g)以下であり、pHが2.0以上4.5以下の範囲内の酸性を呈するカーボンブラックである。酸化チタンやベンガラのごとき無機顔料は静置や比較的穏やかな流動場面で安定な微細分散は可能であるが、本発明の目的には、種々の工夫をこらしても印刷流路の閉塞が起こり不適当であった。カーボンブラック顔料といえどもD B P吸油量が15以上180 (ml/100g)以下の範囲内のもので、しかもpHが2.0以上4.5以下の範囲内の酸性を呈するカーボンブラックを用い、インク中で顔料粒子の9.0 Wt%以上が粒径0.01 μm以上1.0 μm以下であって、平均粒径が0.02 μm以上0.5 μm以下の範囲内にあって、後述の有効な分散剤を含む特定有機媒体中に安定に分散している場合において印刷流路の閉塞が起こらず、鮮明な印刷が可能であった。吸油量が上記範囲を逸脱すると分散剤配合量の増大や印刷濃度の低下を犠牲にする顔料配合量の低下等の工夫を図っても印刷流路の閉塞が起こりやすくなるし、粒径やpHが上記範囲を逸脱すると印刷流路の閉塞が起こったり鮮明な印刷ができなくなる場合が多くなって不適当である。またこの様な条件を満たさないとインクの長期保管時の微細安定性の確保が不十分で使用に難がある。なおD B P吸油量やpHは、当業界において周知の粉粒体の性状に関わるパラメータであり、例えばpHはJ I S-K 6 2 2 1に従って測定される値である。以上のような観点から特に好ましい範囲は、吸油量が20以上160 (ml/100g)以下で、pHが2.5以上4.0以下の範囲内の酸性を呈するカーボンブラックを用い、インク中で顔料粒子の9.9.0 Wt%以上が粒径0.03 μm以上0.8 μm以下であって、平均粒径が0.04 μm以上0.5 μm以下の範囲内にあって安定に分散している場合である。

【0012】本発明のインクにおいて、カーボンブラックは先述の条件を満たせばそれがチャネルブラックかファーネスブラックのいずれであるかを問うことなく実施

可能である。また、微妙な色調の調整等の目的で、カーボンブラックに比較的少量の有機顔料を1種または2種以上を併用することが可能である。本発明で実施可能な顔料としては、アゾ系顔料、縮合アゾ系顔料、フタロシアニン系顔料、アントラキノン系顔料、ペリレン顔料、ペリノン顔料、キナクリドン顔料、ジオキサジン顔料等の顔料から、インクジェットインクの色調以外の特性を損なわない範囲で、その種類と量を選んで併用することが可能である。

【0013】本発明のインク組成における分散媒はエチレンオキサイド鎖またはプロピレンオキサイド鎖の重合度が2以上4以下のポリエチレングリコールのモノブチルエーテルまたはプロピレングリコールのモノブチルエーテルからなる群から選ばれた1種、あるいはそれらの2種以上の混合物である。すなわち、ジエチレングリコールモノブチルエーテル、トリエチレングリコールモノブチルエーテル、ジプロピレングリコールモノブチルエーテル、トリプロピレングリコールモノブチルエーテル、テトラプロピレングリコールモノブチルエーテルからなる群から選ばれた1種、あるいはそれらの2種以上の混合物である。顔料が先述のカーボンブラックである場合に、この分散媒体が、後述の樹脂系分散剤とともに組み合わせて用いられることで本発明の目的が達せられるのである。

【0014】直鎖状あるいは分岐状の飽和脂肪族アルコールを分散媒として使用を試みても、印刷流路の閉塞が起こりインクの噴射が停止し継続的な印刷が不可能であった。なかでも炭素数の大きな直鎖状飽和脂肪族アルコールは常温で結晶化するので、流路を加熱下に保っても印刷流路の閉塞が起こった。ただし、アルコール類の中で例外的にオレイルアルコールは有望であったが、長時間の噴射とりわけ中断を伴う長期の印刷においてインク流路の閉塞が起こった。オレイン酸等の不飽和脂肪酸やそのエステル類、あるいは比較的低分子量のポリアルキレングリコールや本発明に規定する特定のポリアルキレングリコールのモノブチルエーテル以外のグリコールエーテル類、その他顔料インクの分散媒として知られる各種溶剤を、顔料の種類や分散方法また併用する分散剤の種類や配合割合を変えながら検討したが、安定で長期の印刷が可能な媒体として有用な物は見いだせなかった。静置や比較的穏やかな振動下に保管されたインクでは安定な微細分散のインクでありながら、印刷試験に供するとインクの噴射停止が起こるのであった。

【0015】その状況を今少し詳しく述べると、印刷時間の経過とともにプリンタヘッドのあるノズルからのインクの噴射量が低下し始め、しかも噴射路が乱れ、暫くしてそのノズルからの噴射が停止し、この現象が同一ヘッド上の他のノズルでも順次発生し、噴射停止のノズル数が拡大するのである。このような現象が起こると、も

はや印刷は不可能である。実用上は長時間にわたってひとつのノズルの噴射停止も起こってはならないのである。ピエゾ素子の振動数を低下させると、印刷試験開始後インクの噴射停止が起こるまでの時間が延びるけれども同様の事態になり、ヘッドの解体清掃を行わねば印刷を再開できない。ピエゾ素子の振動数をさらに低下させると噴射停止が起こるまでの時間がさらに延びるけれども、印刷時のインクの噴射量が不足する分、印刷速度が低下してしまうので、ともにインクとしての実用的な価値が低下する。噴射停止はプリンタヘッドの微細流路における、顔料の凝集や気泡の混入あるいは発生によるものであろうとの推測は可能であるものの、決定的な原因是不明である。印刷時間の経過とともに噴射停止の起こるインクは、長期間保管後により短時間内に噴射停止が起こるようになることも判明した。また、噴射停止の起こらない一連の順調な印刷が可能なインクでも、印刷を終了したのちインクをインクジェットプリンタ内にセットしたまま放置し、ある時間を経過して印刷を再開するとインクが閉塞して噴射しない場合のあることが判明した。

【0016】本発明者らの検討によると、エチレンオキサイド鎖またはプロピレンオキサイド鎖の重合度が2以上4以下のポリエチレングリコールのモノブチルエーテルまたはプロピレングリコールのモノブチルエーテル、あるいはそれらの混合物を媒体とし、しかも顔料と分散媒の選択組み合わせを本発明のようを選択した場合のみ、調製後あるいは長期間保管後のインクが長期間の連続または断続的な印刷が可能であった。この評価方法と評価結果は、段落番号0026以降において詳述する。

【0017】本発明の分散媒のもう他の特徴は、印刷対象面にインク液滴が到達したのち、顔料の拡散浸透を最小限にし、すなわち、印刷像の滲みを最小限にして、しかも顔料粒子の多くを表面に取り残したまま対象面内部へ速やかに浸透するので、印刷像が濃く鮮明に形成でき、印刷後短時間内に接触しても印刷像の乱れが起こらないことである。媒体の蒸発によるインクの乾燥固化ではない、媒体の印刷面内への浸透による顔料固化（本明細書ではこれも「乾燥」と記載する場合がある）が速やかに起こるのである。この印刷に好適な一種のクロマトグラフィックな効果は予期しない発見であった。この効果は対象面の材質や構造、使用顔料の種類や性状、分散剤の種類や配合比等によってその程度に幾分かの差違があるが分散媒の選択が決定的であった。他種分散媒では、例えばグリコールエーテル類であっても、その分子量が本発明の特定のグリコールエーテルよりも小さいと乾燥は速いが安定な噴射ができないし、分子量が大きいとインクの粘度が高いせいか安定な噴射ができないし、また芳香環含有媒体、例えばビスアルキルフタレート等では、滲みも乾燥も不満足な場合が多く認められ、不適当であった。本発明における分散媒体であるモノブチル

エーテルグリコールは、単独あるいはそれらの混合物で実施可能で、それらの間に揮発性や浸透性での差異はあるが、他種媒体を用いる場合の長期分散安定性の差異に比較して、その差異は小さく問題にならない。

【0018】本発明のインク組成における分散剤は、先述の顔料を分散媒に微細にかつ安定に分散しうる安全な物質であれば良い。一般的に顔料を媒体中に分散させるための分散剤として、数多くの物質が提案されているが、顔料と分散媒の組合せを限定すると有効な分散剤は案外少なく、しかも顔料と分散媒の組合せによって有効な分散剤の種類は異なるのである。しかし、当該分野の技術者は、労力さえいとわなければ有効な分散剤の実験による選定は可能である。本発明者らの検討によると、界面活性剤としても分類される各種の物質で、本発明の顔料と分散媒の組合せで顔料を微細にかつ安定に分散しうる物質は見いだせなかつた。

【0019】一方、界面活性作用のないかあるいは少ない樹脂系化合物の中に、本発明の目的に適う物質のあることが判明した。すなわち、エチレンオキサイド-プロピレンオキサイド共重合体、脂肪族ポリエステル、アミン成分で変性した脂肪族ポリエステル、アミン成分やポリエーテル成分で変性したシリコン樹脂、ポリビニルブチラール、各種アクリル共重合体等が安定な微細分散に有効であった。一方一般的に分散作用があるといわれている物質のなかにもエチルセルロース等のごとく有効でない物質も多々存在するのである。しかも有効であった分散剤のなかでも、ポリビニルブチラールのように比較的低分子量品でなければインクの粘度が高くなるためインクジェットプリンタ用インクとしては使い辛いインクにしかならない物質もある。エチレンオキサイド-プロピレンオキサイド共重合体、脂肪族ポリエステル、アミン成分で変性した脂肪族ポリエステル、アミン成分やポリエーテル成分で変性したシリコン樹脂では、本発明の目的に適うインクが可能であった。以上に例示した化合物以外にも本発明で実施可能な分散剤は存在しうるであろうが、静置や比較的緩やかな振動下に保存しつつ観察して安定な微細分散が確保でき、しかもピエゾ方式のインクジェットプリントで継続して滲みのない鮮明な印刷の可能な分散剤を選んで使用すれば良いのである。なお、当該技術分野でよく行われるところの、分散剤の効果をより高く発揮させるための少量の分散助剤の併用は、本発明においても可能である。分散助剤として各種の界面活性剤、有機塩基性物質等がその例としてあげられ、使用顔料の種類に応じて有効なものとその量を適宜選定して、分散剤の一部として併用することができる。また、分散助剤の併用にあたって、計量や取扱いの便宜のため比較的少量の希釈剤を用いることは、本発明のインクの特性を損なわないかぎり実施可能である。同様に、分散剤の化学的安定性確保のため等の目的で、分散剤樹脂用の少量添加物を含む分散剤も、本発明のインク

の特性を損なわないかぎりにおいて実施可能である。

【0020】着色剤と有機分散媒体および分散剤を必須成分とする本発明のインクジェットプリンタ用溶剤系黒色顔料インクにおいて、必須成分の配合比は、インクの必須成分100重量部あたり、顔料が1.0重量部以上15.0重量部以下、分散剤が使用する顔料の0.1重量倍以上2.0重量倍以下、残余が分散媒である。顔料の種類によって異なるが、顔料配合比が上記の値より過小ではインクの着色濃度が明らかに不十分で実用性に乏しくなるし、過大ではインクの流動性が悪化し、とくにプリンタヘッド内での流動性に支障をきたし不適当である。分散剤の種類によって幾分異なるが、分散剤の配合比が上記の値より過小では顔料の微細で安定な分散が明らかに確保し難いし、過大ではもはや顔料分散への寄与の増大はないし、しかもインクの粘度が高くなりプリンタヘッド内での流動性に支障をきたし、かつインクの印刷対象面での乾燥速度が遅くなつて不適当である。以上の観点から、より好適な配合比はインクの必須成分100重量部あたり、顔料が5.0重量部以上12.0重量部以下、分散剤が使用する顔料の0.2重量倍以上1.5重量倍以下、残余が分散媒の場合である。本発明のインクは上記必須成分の配合に、必要に応じて先述あるいは後述の少量の添加剤成分を加えた組成物である。

【0021】本発明のインクジェットプリンタ用溶剤系顔料インクにおいて、必須成分のみからなるインクはニュートン流動性の低粘度分散液である。インクの粘度は顔料や分散剤の種類や配合比等によって異なるが、概して言えば、20°Cで10~100cps、60°Cで1~20cpsである。顔料の微細で安定な分散が確保されているので粘性も経時に安定である。しかも粘性の温度による変化が小さいので、プリントヘッドの環境温度変化によるインクの噴射調子の変動が少ない。逆に、微妙な噴射調子の変動をなくすためプリントヘッドとその近傍のインク流路を加熱して、常温以上の例えは100°Cにいたる温度範囲で使用に供することができる、とくに当該温度範囲内のある一定温度に保たれた状態にて使用に供することが好ましい。

【0022】本発明のインクの製造方法を例示すると概略以下のようになる。顔料、分散剤、および分散媒の所定量を計量し、攪拌混合したのち、ビーズミルや3本ロールミル等当該分野で周知の分散機にて、顔料の磨碎と微分散化を行つてインクとする。出発原料の顔料は、通常一次粒子の多数個が凝集した二次粒子からなる粉体であり、これを上述のように湿式で二次粒子を磨碎して、より微細な粒子にするとともに分散媒中に分散させるのである。磨碎と微分散化を同時に実行するので、単に分散工程とか分散すると称している。分散工程の条件を変えることにより分散した顔料粒子径とその分布を所望の値にすることが可能である。分散をより効果的に行うため、分散媒を所定量より少なく使用して分散し、得られた濃

厚分散液に残りの分散媒を追加して分散を完了し、所望の組成比のインクとするのもよく行われる方法であり、本発明においても実施可能である。分散工程において微量ながら磨碎不十分の粗大粒子がある場合には、これを遠心分離等の方法で除去するとか、正常に製造できたインクの粘度を特定の目的のために若干低目に修正するときに、分散媒を追加するとか、分散媒と相溶性のしかも分散に悪影響を及ぼさない溶剤すなわち粘度調節溶剤を添加するとか、先述の分散助剤を併用するとか、あるいはインクの製造または使用条件によって消泡剤の添加が望ましい場合には適当な消泡剤を添加する等の修飾は、本発明のインク製造のしかるべき段階において適宜実施可能である。

【0023】本発明のインクにおいて、必要に応じて粘度調節剤として使用可能な溶剤は多種のものがあるが、トリエチレングリコールやトリプロピレングリコール等のグリコール類、メチルーあるいはエチルセロソルブ、メチルーあるいはエチルカルビトール、トリーまたはテトラエチレングリコールのモノプロピルエーテル等のグリコールエーテル類、オレイン酸オクチルやソルビタンモノラウレート等の脂肪酸エステル類等がその例として挙げられる。その添加量はインクの粘度以外の印刷特性の変化が許容される程度に止めるべきで、インクの必須成分の高々20wt%以下である。より低粘度化を望む場合はインクの必須成分の分散媒の配合比を高目に修正して新たなインクを調製するのが良い。本発明のインクにおいて必要に応じて添加可能な消泡剤としては、ポリシリキサン、共重合等による変性ポリシリキサン等が例示される。その添加量はインクの1wt%程度以下で十分である。また、印刷対象面へのインクの固着強度を高めるためにシランカップリング剤やチタンカップリング剤がインクに添加されることがあるが、本発明においても必要に応じてカップリング剤の添加が可能であり、添加量はインクの1wt%程度以下で十分である。

【0024】以上に述べたように本発明は、着色剤として特定のカーボンブラック顔料を、分散媒体として特定のグリコールエーテルを、分散剤として有効な樹脂系化合物を組み合わせて用いることにより、顔料が微細な粒子として分散し、インクジェットプリンタ内部の細隙を容易に通過し、かつ長期の放置や保存によって粒子が凝集しないこと、ならびに印刷後滲むことなく短時間に乾燥して、高速の印刷が可能なインクジェットプリンタ用溶剤系顔料インクを提供するものである。本発明のインクは、印刷・情報用紙、包装用紙、段ボール原紙やその表装紙、白板紙等の紙類、あるいは広くベニヤ板や合板と呼ばれている木質の浸透性材料の表面に、インクジェットプリント方式とくにピエゾ方式で印刷するのに適している。印刷像は各種の文字や数字、バーコードやロゴマーク等の図形、各種の絵柄、ポスター等インクジェットプリンタで印刷可能なものすべてが可能である。

【0025】以下、本発明について実施例を挙げてより詳細に説明する。実施例中での部は重量部である。インクの調製では、予定の分散媒の2/5量を用いてビーズミルで分散し、濃厚インクを取り出したのち濃度調整を兼ねて残りの分散媒を攪拌下に加えて、所定配合比のインクとした。インク中の顔料粒子径はレーザードップラ効果の周波数解析を行う動的光散乱法で測定した。インクの粘度はB型粘度計を用い、20°Cおよび60°Cで測定した。インクの表面張力はウィルヘルミー式表面張力計で室温にて測定した。

【0026】インクのインクジェットプリント試験は、ピエゾ素子1個当たり3個のインク噴出孔を持つノズルが30個直列に配置されたプリントヘッドを用い、噴出孔の開口径は50μm、インクは1本のパイプでヘッドに導かれた後ヘッド内で30個のノズルに分岐しそれぞれが3個のインク噴出孔に通じていて、流路のもっとも狭いところの径は100μmである。ノズルは60°Cの恒温状態に保った。インク噴射のためのピエゾ素子の振動周波数(以下印刷周波数と言う)は10000Hzから8000Hzまで1000Hz刻みで順次変化させる。当試験では少なくとも30分以上安定に全ノズルから継続して、順調にインクの噴射が行える限界の印刷周波数(限界印刷周波数)を求める。なお、当試験機で限界印刷周波数が1000Hzあるいはそれ以下であっても印刷の可能なインクと見なしうるが、高速の印刷をみこす社会の趨勢からすると3000Hz以上の限界印刷周波数が望ましい。浸透性の印刷対象面としては、コピー用紙、段ボール原紙上のクラフト紙、白板紙、ベニヤ板を用い、これを移動させながら印刷して、インクが途切れることなく一定幅の線状に順調に噴射されているかどうか、また印刷後短時間内の接触で印刷像が乱れるか否か、接触せずに放置して印刷像の滲みの程度を目視で観察した。インク中の顔料の分散安定性をみるため、インクを解放容器中常温で30日間保存したのち上記印刷試験を行うインクの常温保存安定性試験、インクを密栓容器中、80°Cの空気浴中に14日間保存したのち常温に戻し、上記印刷試験を行うインクの熱時保存安定性試験、インクを80°Cの空気浴中に14時間置き、ついで-20°Cの空気浴中に12時間置くことを5回繰り返したのち印刷試験を行うインクの熱サイクル安定性試験と、印刷試験機にインクを充填したまま24時間印刷を停止したのち印刷を再開する印刷中断再開試験を適宜実施した。

【0027】

【実施例】(実施例1)顔料としてDBP吸油量が90(mL/100g)、pHが3.0のチャネルカーボンブラック(C.I.No.77266:デグサ社製スペシャルブラック4A)8.0部、分散剤としてエチレンオキサイド-プロピレンオキサイドブロックコポリマ7.0部、分散媒としてトリエチレングリコールモノブチルエーテル84.8

部、ジエタノールアミン0.2部からなるインクを調製した。インク中で顔料粒子の9.9.5Wt%以上が粒径0.01μm以上1.0μm以下であって、平均粒径が0.05μmであった。粘度は20℃で62cps、60℃で17cps、表面張力は31(mN/m)であった。印刷試験において限界印刷周波数は6000Hzであり、各印刷対象面上に印刷後短時間内の接触で印刷像が乱れることなく、滲みのない安定で高速の印刷ができた。インクの常温保存安定性試験、熱時保存安定性試験、熱サイクル安定性試験後の印刷試験、印刷中断再開試験でも同様の良好な結果をえた。

【0028】(比較例1)実施例1の顔料をDBP吸油量が178(ml/100g)、pHが5.0であるファーネスカーボンブラック(C.I.No.77266:キャボット社製VULCAN XC-72R)に替えて実施例1の方法を繰り返し、インクの調製と印刷試験を行った。インク中で顔料粒子の9.9.5Wt%以上が粒径0.04μm以上1.0μm以下であって、平均粒径が0.08μmであった。粘度は20℃で35cps、60℃で15cps、表面張力は31(mN/m)であった。印刷試験に先立つインクの保存安定性試験や熱サイクル安定性試験で顔料の微細な分散に変化は認められなかったが、調製後のインクの印刷試験において、印刷周波数1000Hzでも15分間の印刷の間に9個のノズルでインクの噴射が停止した。

【0029】(比較例2)実施例1の顔料をDBP吸油量が95(ml/100g)、pHが9.0であるファーネスカーボンブラック(C.I.No.77266:デグサ社製プリンテックス90)に替えて実施例1の方法を繰り返し、インクの調製と印刷試験を行った。実施例1と同様の微細な分散が可能であったが、印刷試験に先立つインクの熱時保存安定性試験や熱サイクル安定性試験で顔料の分散に僅かながら凝集沈降の傾向が認められた。調製直後のインクの印刷試験において、印刷周波数1000Hzで2分間の印刷の間に13個のノズルでインクの噴射が停止した。インクの常温保存安定性試験後の印刷試験においても同様の不満足な結果であった。

【0030】(比較例3)実施例1の分散媒をトリエチレングリコールモノメチルエーテルに替えて実施例1の方法を繰り返し、インクの調製と印刷試験を行った。実施例1と同様の微細な分散が可能であったが、調製直後のインクの印刷試験において、印刷周波数1000Hzで5分間の印刷の間に15個のノズルでインクの噴射が停止した。熱時保存安定性試験後の印刷試験において、印刷周波数1000Hzで2分間の印刷の間に13個のノズルでインクの噴射が停止した。

【0031】(比較例4, 5, 6)実施例1の分散剤をそれぞれノニオン系界面活性剤(第一工業製薬(株)製ノイゲンEA-170)、アニオン系界面活性剤(第一工業製薬(株)製ハイテノール-NO8)、カチオン系界面活性剤(花王(株)製アセタミン-86)のいずれかに

替えて、実施例1の方法を繰り返し3種のインクを調製した。調製後短時間内に顔料の凝集が進み始める認め、実際に微細分散ができなかった。

【0032】(実施例2)実施例1における分散媒をトリエチレングリコールモノブチルエーテルに替えて実施例1の方法を繰り返した。限界印刷周波数が8000Hzであること以外は、実施例1と同様の結果をえた。

【0033】(比較例7)実施例2の分散媒をトリエチレングリコールモノエチルエーテルに替えて実施例2の方法を繰り返し、インクの調製と印刷試験を行った。実施例2と同様の微細な分散が可能であったが、調製直後のインクの印刷試験において、印刷周波数2000Hzで10分間の印刷の間に10個のノズルでインクの噴射が停止した。熱時保存安定性試験後の印刷試験において、印刷周波数1000Hzで3分間の印刷の間に15個のノズルでインクの噴射が停止した。インクの常温保存安定性試験後の印刷試験においても同様の不満足な結果であった。

【0034】(実施例3)顔料としてDBP吸油量が100(ml/100g)、pHが3.5であるファーネスカーボンブラック(C.I.No.77266:三菱化学(株)製MA-100)9.0部、分散剤としてC18オキシカルボン酸ポリエステル8.0Wt%と、その助剤である界面活性剤のステアリン酸アミド塩酸塩1.0Wt%、同ステアリルアルコールサルフェートNa塩1.0Wt%からなる混和物の9.0部と、分散媒であるジプロピレングリコールモノブチルエーテル82.0部とからなるインクを調製した。なお、インクの調製途中でチタンカップリング剤の0.05部を少量の揮発性溶剤とともに添加した。インク中で顔料粒子の9.9.4Wt%以上が粒径0.03μm以上1.0μm以下であって、平均粒径が0.06μmであった。粘度は20℃で65cps、60℃で15cps、表面張力は35(mN/m)であった。印刷試験において限界印刷周波数は6000Hzであり、各印刷対象面上に印刷後短時間内の接触で印刷像が乱れることなく、滲みのない安定で高速の印刷ができた。印刷周波数を7000Hzにすると、印刷開始後5~8分後に3個のノズルでインクの噴射が停止したが、その後新たなインクの噴射停止は起こらなかった。インクの常温保存安定性試験や熱時保存安定性試験および熱サイクル安定性試験後の印刷試験でも、また印刷中断再開試験でも同様の良好な結果を得た。

【0035】(比較例8)実施例3の分散媒をジプロピレングリコールモノメチルエーテルに替えて、実施例3の方法を繰り返した。インク中で顔料粒子の9.9.5Wt%以上が粒径0.02μm以上1.0μm以下であって、平均粒径が0.06μmであった。粘度は20℃で70cps、60℃で20cps、表面張力は34(mN/m)であった。インクの熱時保存安定性試験や熱サイクル安定性試験で顔料の微細な分散に変化は認められな

かつたが、調製後のインクの印刷試験において印刷周波数2000Hzでも10分間の印刷の間に15個のノズルでインクの噴射が停止した。

【0036】(実施例4) 顔料としてD B P吸油量が90(m1/100g)、pHが3.0のチャネルカーボンブラック(C. I. No. 77266: デグサ社製 スペシャルブラック4 A) 7.0部、分散剤としてアミノ基とポリエーテル基で変性したシリコン樹脂(信越化学工業(株)製 X-22-3939A) 8.0部と、分散媒であるジエチレングリコールモノブチルエーテル85.0部とからなるインクを調製した。インク中で顔料粒子の9.3Wt%以上が粒径0.03μm以上1.0μm以下であって、平均粒径が0.08μmであった。粘度は20℃で13cps、60℃で6cps、表面張力は31(mN/m)であった。印刷試験において限界印刷周波数は6000Hzであり、各印刷対象面上に印刷後短時間内の接触で印刷像が乱れることなく、滲みのない安定で高速の印刷ができた。インクの常温および熱時保存安定性試験や熱サイクル安定性試験後の印刷試験でも、印刷中断再開試験でも同様の良好な結果をえた。

【0037】(比較例9) 実施例4における分散媒をジエチレングリコールモノブチルエーテルモノアセテートに替えて、実施例4の方法を繰り返した。実施例4の場合と同様に微細分散のインクが調製でき、インクの常温および熱時保存安定性試験や熱サイクル安定性試験で顔料の微細な分散に変化は認められなかつたが、調製後のインクの印刷試験において、印刷周波数1000Hzでも10分間の印刷の間に18個のノズルでインクの噴射が停止した。

【0038】

【発明の効果】本発明は、着色剤として特定のカーボンブラック顔料を、分散媒体として特定のグリコールエーテルを、これらに有効な樹脂系化合物を選択組み合わせることで、顔料が微細な粒子として分散し、インクジェットプリンタ内部の細隙を容易に通過し、かつ長期の放置や保存によって粒子が凝集しないこと、ならびに印刷後滲むことなく短時間に固化して浸透性対象面に対して、高速の印刷が可能なインクジェットプリンタ用溶剤系黒色顔料インクを提供することができた。

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-220527

(43)Date of publication of application : 14.08.2001

(51)Int.Cl.

C09D 11/00

(21)Application number : 2000-033305

(71)Applicant : FUJI SHIKISO KK

(22)Date of filing : 10.02.2000

(72)Inventor : KONISHI HIDEKI
SUZUKI TAKASHI

(54) SOLVENT-BASE BLACK PIGMENT INK FOR INK JET PRINTER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an ink composition which is prepared by using a carbon black pigment and makes high-speed, and high-definition ink jet printing on a permeable material possible.

SOLUTION: In preparing a solvent-base black pigment ink for ink jet printing comprising a colorant, an organic dispersion medium, and a dispersant, a specific pigment is used as the colorant; a specific glycol ether is used as the dispersion medium; and a resinous compound effective as a dispersant for them is used. Thus is provided an ink composition in which the pigment disperses well as fine particles and can pass through narrow passages in a printer; in which particles do not agglomerate even when kept standing or stored for a long time; and of which the medium permeates quickly into a permeable material after printing, solidifying the composition without causing blur.

* NOTICES *

**JPO and NCIP are not responsible for any
damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. **** shows the word which can not be translated.

3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] In the solvent system black pigment ink for ink jet printers which uses a pigment, an organic dispersion-medium object, and a dispersant as an indispensable component DBP oil absorption is below or more 15 180 (ml / 100g) as a pigment. The carbon black which pH presents the acidity within the limits of 4.5 or less [2.0 or more] One sort chosen from the group which the degree of polymerization of an ethyleneoxide chain or a propylene oxide chain becomes from the monobutyl ether of or more 2 four or less polyethylene glycol, or the monobutyl ether of a polypropylene glycol as a dispersion-medium object of a pigment, Or the thing a resin system compound effective in the combination of the above-mentioned coloring agent and a dispersion medium as a dispersant is used [thing] for two or more sorts of those mixture, And solvent system black pigment ink for ink jet printers which more than 98.0Wt% of a pigment particle is 1.0 micrometers or less

in 0.01-micrometer or more particle size, and is characterized by for mean particle diameter being within the limits of 0.02 micrometers or more 0.5 micrometers or less, and distributing to stability.

[Claim 2] Less than [of the pigment which a dispersant uses / per indispensable component 100 weight section of ink, and a pigment / below the 15.0 weight sections more than the 1.0 weight section / more than 0.1 weight twice 2.0 weight twice], solvent system black pigment ink for ink jet printers according to claim 1 whose remainder is a dispersion medium.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the solvent system pigment ink at the time of printing with an ink jet printer to permeability ingredient sides, such as paper and timber.

[0002]

[Description of the Prior Art] The printing technique of an ink jet print method is developed in recent years, and, generally it began to be used widely. Although various methods were proposed and the utilization phase is reached, it is common in them to inject at high speed and to make an image from ink to an object side, forming a detailed liquid ink drop. Since it is made to dissolve in various media and deals in a color as a coloring agent of ink, it is suitable for injecting forming a drop detailed as ink in a uniform dissolution condition. However, a color has a difficulty in lightfastness or a water resisting property, and the aspect of affairs of an activity has constraint. On the other hand, since the pigment is excellent in lightfastness or a water resisting property, it is desirable, but since there is no medium which dissolves it, it must be used as dispersion liquid of a very fine particle. It is the indispensable conditions for pigment ink that the supply way of the ink which results in the nozzle and nozzle of a printer head from the demand of a print quality is detailed, and the particle diameter of the pigment which passes through that is still more detailed, and that must not condense at the time of an activity and storage, must not sediment, namely, a detailed distributed condition is maintained at stability. Although practical use is presented with pigment ink in some fields, since stable detailed distribution of a pigment which bears the severe condition of an ink jet print is difficult, the pigment ink in the field concerned is not yet put in practical use. The fate which becomes severer has a demand in the more minute ink [in / a high speed or if printing of a large area is called for more at all / more / an ink jet print] of endurance more like other print processes.

[0003] Although pigment ink for ink jet printers is desired for such a background, since the lightfastness of a pigment and a water resisting property have desiccation of ink or the slow solidification rate, and the printing image immediately after printing is confused by contact or they have many cases where the device for distribution becomes an enmity and the water resisting property of a print is inferior, in drainage system distribution of a satisfactory good thing, the pigment-content powder in a non-drainage system is desirable. Moreover, among nonaqueous dispersion media, although a volatile solvent can expect desiccation solidification of the prompt ink by evaporation of the solvent after printing, it takes place [change of the presentation by volatilization / tend] at the times of handling, such as the time of printing, and is unsuitable. If the interior of paper or the woody field for permeability is permeated promptly and ink solidifies with the solvent of comparatively difficulty volatility at the time of printing, a pigment will be spread on an object side front face, a printing image will spread by contact, or it will not be confused, and it will be assumed that minute printing is possible. It seems to be whether ink permeates the detailed part of a print head well, and this can supply ink certainly, and a problem of the same kind. It seems that however, there is no knowledge what kind of dispersion medium can respond to high-speed printing more by combining stable detailed distribution and such a good osmosis fluidity in relation by the pigment or the dispersant.

[0004]

[Problem(s) to be Solved by the Invention] Development of the pigment ink for ink jet printers which carried out detailed distribution of the pigment at the dispersion medium of a non-drainage system which secures both the osmosis fluidities of detailed stable distribution of a pigment, and ink.

[0005]

[Means for Solving the Problem] The object achievement is expected by selection of a new ink presentation or a compounding ratio.

[0006] Since the ink jet print method optimal as an object is a piezo method which performs the formation of a detailed drop and injection of ink by the piezo-electric element when aiming at development of the pigment ink for ink jet printers which carried out detailed distribution of the pigment to the dispersion medium of a non-drainage system, the method will be made into an example and the content of this invention will be stated more to a detail. By the piezo method, electric oscillation is changed into a dynamics oscillation, it tells ink, ink is turned to an object side from two or more holes with a detailed nozzle, and it injects as a detailed drop. Injection of a detailed drop is controlled by the electric-oscillation input to a piezo-electric element, controls the attainment location of the ink on an object side by migration of an object side or a printer nozzle, and draws a desired image. A piezo-electric element is arranged in dozens of micrometer or more location to which it is about hundreds of micrometers and opening of some holes is usually expected in the medium, and, as for the path of the supply way of the ink in which the diameter of opening of the hole of a nozzle usually reaches dozens of micrometers and there, dozens of components are usually arranged from some with the whole nozzle. Since opening and the passage of the neighborhood of it are detailed, naturally stable detailed distribution of a pigment becomes an indispensable condition.

[0007] Although a certain amount of guess was possible, and the ink there is no change in the viscosity of the detailed distributed condition of a pigment or ink, and it is considered that is stability was prepared when actually saved under heating or a heat cycle when it was the simple problem into what kind of combination a pigment, a dispersion medium, and a dispersant should have been made in pigment ink other than for ink jet printers, the ink which was able to be printed favorably at the beginning of printing test initiation stops [injection of ink] after a while. That is, the scale taken in development of conventional various ink is not helpful. When printing of long duration was not completed in a practical print speed although the continuity of injection of ink with the device of a dispersant improved to some extent when the solvent with the high hydrophilic property which has water and compatibility, for example according to other examination of this invention persons was made into the dispersion medium, and the hydrophobic, strong solvent was made into the dispersion medium, even if it devised various dispersants, injection of ink was unsuitable like the above-mentioned. That is, with neither the single scale of a hydrophilic property or hydrophobicity, nor the single scale of a dispersant, solution is in prospect. If it says whether ink is equal also to the high-speed oscillation of thousands of Hz of the piezo-electric element at the time of printing, and detailed passage may be flowed through to stability, and whether many demands which are described below can also be filled simultaneously, in well-known knowledge, the guide of solution will not be acquired conventionally.

[0008] The ink the quantity of was decreased by injection is supplied from an ink reservoir of the supply way other end by the capillarity in the supply way which is a capillary. The surface tension and the viscosity property of ink must be chosen for supplying the ink to the head of a nozzle smoothly. Although it is generally so advantageous to capillarity that surface tension is large, when first filled up with ink, air bubbles are generated in passage or it is easy to remain in it, and while it prints, it is possible [it] to blockade passage. Once it does not ask whether it is based on a condensation pigment, or it is based on air bubbles but blockades, since injection of ink becomes impossible, if the nozzle stops printing and passage of ink is not reashed, it cannot be used any longer. An injection halt took place in many cases, degassing was not able to be beforehand carried out by supersonic vibration, and a solvent independent examined the surfactant as a dispersant of ink, and each-other gap has not improved it, either. When the viscosity of ink is too high, its drift velocity is slow, high-speed floating in the capillary corresponding to the injection performed at high speed is

impossible, supply of ink cannot be followed, if too low, overflow will be carried out from a nozzle, the ink of a printing image will be superfluous and it will be confused. Moreover, before the argument of the absolute value of viscosity, if viscous behavior is not a Newtonian flow, inconvenience will arise. Surface tension and a viscosity property are also likely to influence thin drop-ization of the injected ink, and are likely to have the range suitable for forming the drop of proper magnitude, in view of the printing image. However, it is specifically unknown.

[0009] Two or more drops of the injected ink form the printing image of the line breadth beyond it from a submillimeter meter on an object side at the time of cm. Line breadth and its intermittence length are controlled by actuation of a piezo-electric element. Since the object sides of printing are paper and a woody permeability side, a dispersion medium needs to be the matter which leaves a pigment to a front face, permeates the interior of a field promptly, and, and a printing image does not spread by contact or is not carried out. [that a pigment is spread on the front face of an object side] Although it is whether ink permeates the detailed part of a print head well, and this can supply ink certainly, and a problem of the same kind, since the nature of a cellulose or others, or a composite organic macromolecule and the composite inorganic quality of packing are contained and it is constituted, the field for printing is not identically discussed to a head being metal.

[0010] As for a loan, the hand of presentation combination which fills many various demands as mentioned above simultaneously is not obtained easily. When oleyl alcohol was chosen as an organic dispersion-medium object as a result of many trial-and-error, this invention person found out that the solvent system pigment ink for ink jet printers could be constituted using various pigments, and already applied as Japanese Patent Application No. 11-209022. However, according to a subsequent examination, although applied ink was excellent in distributed stability or a printing property, it became clear that practically still more advanced distributed stability should have been provided. For this reason, this invention persons continued amelioration research and reached this invention about black ink.

[0011] In the ink presentation of this invention, DBP oil absorption is below or more 15 180 (ml / 100g), and the pigment which is a coloring agent is carbon black which pH presents the acidity within the limits of 4.5 or less [2.0 or more]. Although it was possible, even if the detailed distribution with titanium oxide and the inorganic pigment like red ocher stable in standing or a comparatively quiet floating scene put various creativity on the object of this invention, lock out of printing passage happens and was unsuitable [distribution]. Also although it is called a carbon black pigment, DBP oil absorption is a thing within the limits below or more 15 180 (ml / 100g). And the carbon black which pH presents the acidity within the limits of 4.5 or less [2.0 or more] is used. More than 98.0Wt% of a pigment particle is 1.0 micrometers or less in 0.01-micrometer or more particle size in ink. Mean particle diameter was within the limits of 0.02 micrometers or more 0.5 micrometers or less, when distributing to stability in the specific organic medium containing the effective below-mentioned dispersant, lock out of printing passage did not take place, but clear printing was possible. If lock out of printing passage becomes easy to take place the device of lowering of the pigment loadings at the sacrifice of buildup of dispersant loadings, or lowering of printing concentration when oil absorption deviates from the above-mentioned range etc. as drawing and particle size and pH deviate from the above-mentioned range, in the case where printing clear in lock out of printing passage taking place becomes impossible, it increases and is unsuitable. Moreover, if such conditions are not fulfilled, reservation of the detailed stability at the time of the long-term storage of ink is inadequate, and difficulty is in an activity. In addition, DBP oil absorption and pH are the parameters in connection with the description of a well-known particulate matter in this industry, for example, pH is a value measured according to JIS-K6221. Oil absorption is below or more 20 160 (ml / 100g), and the range especially desirable from the above viewpoints is the case where more than 99.0Wt% of a pigment particle is 0.8 micrometers or less in 0.03-micrometer or more particle size in ink, mean particle diameter is within the limits of 0.04 micrometers or more 0.5 micrometers or less using the carbon black which pH presents the acidity within the limits of 4.0 or less [2.5 or more], and it is distributing to stability.

[0012] Carbon black can be carried out in the ink of this invention, without asking any of channel black or

furnace black it is, if the conditions of point ** are fulfilled. Moreover, it is possible to use together one sort or two sorts or more for comparatively a small amount of organic pigment to carbon black for the object, such as adjustment of a delicate color tone. It is possible to be the range which does not spoil any properties other than the color tone of ink jet ink, and to choose and use the class and amount together as a pigment which can be carried out by this invention, from pigments, such as azo pigment, condensation azo pigment, phthalocyanine pigment, an anthraquinone system pigment, a perylene pigment, a peri non pigment, a quinacridone pigment, and a dioxazine pigment.

[0013] The dispersion mediums in the ink presentation of this invention are one sort chosen from the group which the degree of polymerization of an ethyleneoxide chain or a propylene oxide chain becomes from the monobutyl ether of or more 2 four or less polyethylene glycol, or the monobutyl ether of propylene glycol, or those two sorts or more of mixture. That is, they are one sort chosen from the group which consists of the diethylene-glycol monobutyl ether, the triethylene glycol monobutyl ether, the tetraethylene glycol monobutyl ether, the dipropylene glycol monobutyl ether, the tripropylene glycol monobutyl ether, and the tetrapropylene glycol monobutyl ether, or those two sorts or more of mixture. When a pigment is carbon black of point **, the object of this invention is reached by this dispersion-medium object combining and being used with the below-mentioned resin system dispersant.

[0014] Even if it tried the activity by making the saturation fatty alcohol of the shape of a straight chain, and the letter of branching into a dispersion medium, lock out of printing passage took place, injection of ink stopped, and continuous printing was impossible. Since the straight chain-like saturation fatty alcohol with a carbon number big especially was crystallized in ordinary temperature, even if it maintained passage at the bottom of heating, lock out of printing passage took place. However, although oleyl alcohol was exceptionally [in alcohols] promising, lock out of ink passage took place in long-term printing accompanied by injection division interruption of long duration. Although the various solvents known as unsaturated fatty acid, such as oleic acid, the ester of those or glycol ether other than the monobutyl ether of the specific polyalkylene glycol comparatively specified to the polyalkylene glycol and this invention of low molecular weight, and other dispersion media of pigment ink were examined changing the class of pigment, the distributed approach, and the class and the blending ratio of coal of a dispersant that are used together, the object useful as a medium in which stable long-term printing is possible was not able to be found out. In the ink kept under standing or a comparatively moderate oscillation, though it was ink of stable detailed distribution, when the printing trial was presented, an injection halt of ink took place.

[0015] If that situation is described now somewhat in detail, the injection quantity of the ink from the nozzle which has a printer head with the printing passage of time begins to fall, moreover, the injection from that nozzle will stop after a while, an injection way will carry out sequential generating also with turbulence and the nozzle of the others [phenomenon / this] on the same head, and the number of nozzles of an injection halt will be expanded. If such a phenomenon happens, printing is already impossible. An injection halt of one nozzle must not take place over long duration practically, either. Printing cannot be resumed, if the vibration frequency of a piezo-electric element is reduced, it becomes same situation and overhaul cleaning of a head is not performed, although time amount until an injection halt of the ink after printing test initiation takes place is prolonged. Since the part which runs short of the injection quantity of the ink at the time of printing, and a print speed will fall although time amount until an injection halt takes place is prolonged further if the vibration frequency of a piezo-electric element is reduced further, the practical value as [both] ink falls. The decisive cause is unknown although the guess that an injection halt will be what is depended on condensation of a pigment, or mixing or generating of air bubbles in the detailed passage of a printer head is possible. It also became clear that, as for the ink in which an injection halt takes place with the printing passage of time, an injection halt comes to take place into a short time by the prolonged storage back. Moreover, it became clear that it was in case ink will not blockade and inject it, either, if the ink in which a series of favorable printings to which an injection halt does not take place are possible is also left setting ink in an ink jet printer after ending printing, goes through a certain time amount and resumes printing.

[0016] According to examination of this invention persons, only when the degree of polymerization of an ethyleneoxide chain or a propylene oxide chain moreover chose the selection combination of a pigment and a dispersion medium like this invention through the monobutyl ether of or more 2 four or less polyethylene glycol, the monobutyl ether of propylene glycol, or those mixture, continuation and intermittent printing of a long period of time [ink / after preparation or prolonged storage] were possible. This assessment approach and an assessment result are explained in full detail after the paragraph number 0026.

[0017] Since other descriptions which the dispersion medium of this invention has permeate the interior of an object side promptly, making diffusion osmosis of a pigment into the minimum, namely, making a blot of a printing image into the minimum, and leaving many of pigment particles on a front face moreover after a liquid ink drop arrives at the field for printing, they are that turbulence of a printing image does not take place even if a printing image can form vividly deeply and it contacts in an after [printing] short time. The pigment solidification (on these descriptions, this may also be indicated to be "desiccation") by osmosis into the printing side of a medium which is not desiccation solidification of the ink by evaporation of a medium takes place promptly. a kind of suitable chromatography for this printing – graphic effectiveness was unexpected discovery. Although this effectiveness was boiled to that extent with the construction material and structure of an object side, the class and description of the pigment used, a class, a compounding ratio of a dispersant, etc. and that difference had it a little, its selection of a dispersion medium was decisive. By the other type dispersion medium, even if it was glycol ether, for example, when the molecular weight was smaller than the specific glycol ether of this invention, although desiccation was quick, stable injection was not completed, because the viscosity of ink was high when molecular weight was large, stable injection was not completed, and many cases where a blot and desiccation were dissatisfied were accepted at the ring content medium, for example, bis-alkyl phthalate, and it was unsuitable. As compared with the difference in the long-term distribution stability in that the monobutyl ether glycol which is a dispersion-medium object in this invention is independent, or the case of using an other type medium, although it can carry out with those mixture and the difference in volatility or permeability is among them, the difference does not become a problem small.

[0018] The dispersant in the ink presentation of this invention should just be the safe matter which may distribute [a dispersion medium] the pigment of point ** to stability minutely. As a dispersant for generally distributing a pigment in a medium, although many matter is proposed, if the combination of a pigment and a dispersion medium is limited, there are few effective dispersants unexpectedly and, moreover, the class of effective dispersant changes with combination of a pigment and a dispersion medium. however, the engineer of the field concerned – an effort – **** trap ***** – the selection by experiment of an effective dispersant is possible. According to examination of this invention persons, the matter which may distribute a pigment to stability minutely in the pigment of this invention and the combination of a dispersion medium with various kinds of matter classified also as a surfactant was not able to be found out.

[0019] On the other hand, there is nothing or it became clear that the matter which is a surface activity operation and which suits the object of this invention was in few resin system compounds. That is, an ethyleneoxide-propylene oxide copolymer, aliphatic series polyester, the aliphatic series polyester that denaturalized of the amine component, the silicon resin which denaturalized of the amine component or the polyether component, a polyvinyl butyral, various acrylic copolymers, etc. were effective in stable detailed distribution. The matter which is not effective also exists plentifully like ethyl cellulose etc. also in the matter said for there to be a distributed operation generally on the other hand. And there is also matter which uses as ink for ink jet printers, and becomes only hot ink also in the effective dispersant since the viscosity of ink will become high like a polyvinyl butyral if it is not a low-molecular-weight article comparatively. The ink which suits the object of this invention in an ethyleneoxide-propylene oxide copolymer, aliphatic series polyester, the aliphatic series polyester that denaturalized of the amine component, and the silicon resin which denaturalized of the amine component or the polyether component was possible. Although the dispersant which can be carried out by this invention besides the compound illustrated above may exist, it should just use the possible dispersant of clear printing which observes saving under standing or a comparatively loose

oscillation, can secure stable detailed distribution, moreover continues on the ink jet print of a piezo method, and does not have a blot, choosing it. In addition, concomitant use of a small amount of distributed assistant for demonstrating more highly the effectiveness of the dispersant performed by the technical field concerned being sufficient is possible also in this invention. As a distributed assistant, various kinds of surfactants, the organic base nature matter, etc. can be raised as the example, can select an effective thing and its amount suitably according to the class of pigment used, and can use together as some dispersants. Moreover, in concomitant use of a distributed assistant, using comparatively a small amount of diluent for the facilities of measuring or handling can be carried out, unless the property of the ink of this invention is spoiled. The dispersant which similarly are the objects for chemical stability reservation of a dispersant etc., and contains the little additive for dispersant resin can also be carried out unless the property of the ink of this invention is spoiled.

[0020] In the solvent system black pigment ink for ink jet printers of this invention which uses a coloring agent, an organic dispersion-medium object, and a dispersant as an indispensable component, less than [of the pigment with which a dispersant uses / per indispensable component 100 weight section of ink and a pigment / the compounding ratio of an indispensable component below the 15.0 weight sections more than the 1.0 weight section / more than 0.1 weight twice 2.0 weight twice], and the remainder are dispersion mediums. It causes [if / than the above-mentioned value / too little / a pigment compounding ratio /, the coloring concentration of ink is clearly inadequate and become scarce at practicability, if excessive, the fluidity of ink gets worse, and / the fluidity within a printer head] trouble especially and is unsuitable although it changes with classes of pigment. although it changes a little with classes of dispersant, if it is hard to secure detailed and stable distribution of a pigment clearly if [than the above-mentioned value] too little [the compounding ratio of a dispersant] and excessive — already — buildup of the contribution to pigment-content powder — or moreover the viscosity of ink becomes high, and trouble is caused to the fluidity within a printer head, and the rate of drying in the field for printing of ink becomes late and is unsuitable. It is the case where less than [of the pigment with which a dispersant uses / per indispensable component 100 weight section of ink and a pigment / a more suitable compounding ratio below the 12.0 weight sections more than the 5.0 weight sections from the above viewpoint / more than 0.2 weight twice 1.5 weight twice], and the remainder are dispersion media. The ink of this invention is the constituent which added the little additive component of point ** or the after-mentioned to combination of the above-mentioned indispensable component if needed.

[0021] In the solvent system pigment ink for ink jet printers of this invention, the ink which consists only of an indispensable component is hypoviscosity dispersion liquid of the Newton fluidity. Although the viscosity of ink changes with classes, compounding ratios, etc. of a pigment or a dispersant, it is 1-20cps at 10-100cps and 60 degrees C in 20 degrees C generally. Since detailed and stable distribution of a pigment is secured, viscosity is also stable with time. And since change by viscous temperature is small, there is little fluctuation of the injection condition of the ink by environmental temperature change of a print head. On the contrary, it is possible to present an activity in the temperature requirement which heats the ink passage of a print head and its near in order to lose fluctuation of a delicate injection tune, and results in 100 degrees C beyond ordinary temperature, and it is desirable to present an activity in the condition of having been especially maintained at a certain constant temperature in the temperature requirement concerned.

[0022] It comes to be below an outline when the manufacture approach of the ink of this invention is illustrated. A pigment, a dispersant, and the specified quantity of a dispersion medium are measured, and after carrying out stirring mixing, in the disperser of common knowledge in the fields concerned, such as a bead mill and 3 roll mills, grinding and micro-disperse-izing of a pigment are performed and it considers as ink. The pigments of a start raw material are fine particles which consist of an aggregated particle which many of a primary particle usually condensed, and they are distributed in a dispersion medium while they grind an aggregated particle with wet as mentioned above and make this a more detailed particle. since grinding and micro-disperse-ization are performed simultaneously — only — a distributed process — it has called distributing. It is possible to make into a desired value the pigment particle diameter distributed by changing the conditions

of a distributed process and its distribution. Since it distributes more effectively, the remaining dispersion medium is added to the thick dispersion liquid which distributed using a dispersion medium fewer than the specified quantity, and were obtained, distribution is completed, the approach often performed also considers as the ink of a desired presentation ratio, and it can be carried out also in this invention. When there is a big and rough particle of grinding imperfection with a minute amount in a distributed process When correcting to eye the low one a little the viscosity of the ink which removed this by approaches, such as centrifugal separation, or has been manufactured normally for the specific object Add a dispersion medium, add, the solvent, i.e., the viscosity accommodation solvent, of a dispersion medium and compatibility which moreover does not have an adverse effect on distribution, or The distributed assistant of point ** can be used together, or qualification of adding a defoaming agent suitable when addition of a defoaming agent is desirable can be suitably carried out in the appropriate phase of ink manufacture of this invention according to manufacture or the service condition of ink.

[0023] In the ink of this invention, although a solvent usable as a viscosity modifier is reached at a variety if needed, fatty acid ester, such as glycol ether, such as glycols [, such as triethylene glycol and tripropylene GURIKORURU], methyl - or ethylcellosolve, and methyl - or ethyl carbitol, a tree, or the monopropyl ether of tetraethylene glycol, oleic acid octyl, and sorbitan monolaurate, is mentioned as the example. extent with which, as for the addition, change of printing properties other than the viscosity of ink is permitted – it should stop – the indispensable component of ink – at most – it is less than [20Wt%]. When it desires hypoviscosity-ization more, it is good to correct high the compounding ratio of the dispersion medium of the indispensable component of ink, and to prepare new ink. In the ink of this invention, the denaturation polysiloxane by the polysiloxane, copolymerization, etc. is illustrated as a defoaming agent which can be added if needed. The addition is or less about [of ink] 1Wt%, and is enough. Moreover, although a silane coupling agent and a titanium coupling agent may be added by ink in order to raise the fixing reinforcement of the ink to the field for printing, also in this invention, addition of a coupling agent is possible if needed, and an addition is or less about [of ink] 1Wt%, and is enough.

[0024] As stated above, this invention a specific carbon black pigment as a dispersion-medium object as a coloring agent by using specific glycol ether combining the effective resin system compound as a dispersant A pigment distributes as a detailed particle, the slit inside an ink jet printer is passed easily, and a particle does not condense by long-term neglect or preservation, And it dries for a short time, without spreading after printing, and the solvent system pigment ink for ink jet printers which can print high-speed is offered. The ink of this invention fits the front face of papers, such as printing and an information form, a package form, a liner and corrugating medium, and the mounting paper, a white board, or the woody permeability ingredient currently widely called plywood and a plywood printing by the ink jet print method, especially the piezo method. All the things that can be printed with ink jet printers, such as graphic forms, such as various kinds of alphabetic characters, a figure, a bar code, and a logo mark, various kinds of patterns, and a poster, are possible for a printing image.

[0025] Hereafter, an example is given about this invention and it explains to a detail more. The section in the inside of an example is the weight section. In preparation of ink, the bead mill distributed using 2/5 amount of the dispersion medium of a schedule, and after taking out thick ink, in addition to the bottom of stirring, the remaining dispersion medium was used as the ink of a predetermined compounding ratio to serve also as concentration adjustment. The pigment particle diameter in ink was measured by the dynamic light scattering which performs frequency analysis of the laser-doppler effectiveness. The viscosity of ink was measured at 20 degrees C and 60 degrees C using the Brookfield viscometer. The surface tension of ink was measured at the room temperature with the WIRUHERUMI type surface tension balance.

[0026] After the diameter of opening of a blowout hole was led to 50 micrometers in one pipe and ink is led to a head using the print head by which the nozzle in which the ink jet print trial of ink has three ink blowout holes per piezo-electric element has been arranged at the 30-piece serial, it branches for 30 nozzles within a head, each leads to three ink blowout holes, and the path of the narrowest place of passage is 100 micrometers. a

nozzle – 60-degree C constant temperature – it maintained at the condition. Sequential change of the oscillation frequency (henceforth a printing frequency) of the piezo-electric element for ink injection is carried out by 1000Hz unit from 1000Hz to 8000Hz. In this trial, it continues from all nozzles to stability at least 30 minutes or more, and asks for the printing frequency (marginal printing frequency) of the limitation which can inject ink favorably. in addition, although it can be regarded as the possible ink of printing even if a marginal printing frequency is less than [1000Hz or it] in this testing machine, the marginal printing frequency of 3000Hz or more is desirable, considering the trend of the society which sees and exceeds high-speed printing. It was left as a field for printing of permeability, without whether it is favorably injected by the line of constant width, without printing moving this using a copy paper, the kraft paper in the corrugated fiberboard Hara paper, a white board, and plywood, and ink breaking off, whether a printing image is confused by the contact in an after [printing] short time again, and contacting, and extent of a blot of a printing image was observed visually. The ordinary temperature preservation stability test of the ink which performs the above-mentioned printing trial after saving ink for 30 days in the ordinary temperature in a release container in order to see the distributed stability of the pigment in ink, After saving ink for 14 days during a sealing container and a 80-degree C air bath, it returns to ordinary temperature. The heat cycle stability test of the ink which performs a printing trial after repeating 5 times, placing a preservation stability test and ink subsequently to under a -20-degree C air bath every 14 hours during a 80-degree C air bath for 12 hours at the time of the heat of the ink which performs the above-mentioned printing trial, After suspending printing for 24 hours, filling up a printing testing machine with ink, the resumption trial of printing interruption which resumes printing was carried out suitably.

[0027]

[Example] (Example 1) 90 (ml / 100g) and pH prepared [DBP oil absorption] as a pigment the ethyleneoxide-propylene oxide block-copolymer 7.0 section and the ink in which it consists of the triethylene glycol monobutyl ether 84.8 section and the diethanolamine 0.2 section as a dispersion medium as the channel carbon black (C. special black by I.No.77266:Degussa AG 4A) 8.0 section of 3.0, and a dispersant. More than 99.5Wt% of a pigment particle was 1.0 micrometers or less in 0.01-micrometer or more particle size in ink, and mean particle diameter was 0.05 micrometers. In 20 degrees C, at 62cps and 60 degrees C, viscosity was 17cps and surface tension was 31 (mN/m). Without a marginal printing frequency's being 6000Hz and confusing a printing image by the contact in an after [printing] short time on each field for printing in a printing trial, the blot twisted, it was stable and high-speed printing was completed. The good result with the same said also of the printing trial after a preservation stability test and a heat cycle stability test and the resumption trial of printing interruption was obtained at the time of the ordinary temperature preservation stability test of ink, and heat.

[0028] (Example 1 of a comparison) The pigment of an example 1 was changed to the furnace carbon black (C.I.No.77266: VULCAN XC[by Cabot Corp.]-72R) whose DBP oil absorption is 178 (ml / 100g) and whose pH is 5.0, the approach of an example 1 was repeated, and preparation and a printing trial of ink were performed. More than 99.5Wt% of a pigment particle was 1.0 micrometers or less in 0.04-micrometer or more particle size in ink, and mean particle diameter was 0.08 micrometers. In 20 degrees C, at 35cps and 60 degrees C, viscosity was 15cps and surface tension was 31 (mN/m). Although change was not accepted in detailed distribution of a pigment by the preservation stability test or heat cycle stability test of ink before a printing trial, in the printing trial of the ink after preparation, injection of ink stopped even the printing frequency of 1000Hz with nine nozzles between printings for 15 minutes.

[0029] (Example 2 of a comparison) The pigment of an example 1 was changed to the furnace carbon black (C.I.No.77266: the Degussa AG pudding tex 90) whose DBP oil absorption is 95 (ml / 100g) and whose pH is 9.0, the approach of an example 1 was repeated, and preparation and a printing trial of ink were performed. Although the same detailed distribution as an example 1 was possible, the inclination of flocking settling was slightly accepted in distribution of a pigment by the preservation stability test or the heat cycle stability test at the time of the heat of the ink before a printing trial. In the printing trial of the ink immediately after preparation,

injection of ink stopped with 13 nozzles between printings for 2 minutes with the printing frequency of 1000Hz. Also in the printing trial after the ordinary temperature preservation stability test of ink, it was the same dissatisfied result.

[0030] (Example 3 of a comparison) The dispersion medium of an example 1 was changed to the triethylene glycol monomethyl ether, the approach of an example 1 was repeated, and preparation and a printing trial of ink were performed. Although the same detailed distribution as an example 1 was possible, in the printing trial of the ink immediately after preparation, injection of ink stopped with 15 nozzles between printings for 5 minutes with the printing frequency of 1000Hz. In the printing trial after a preservation stability test, injection of ink stopped with 13 nozzles between printings for 2 minutes with the printing frequency of 1000Hz at the time of heat.

[0031] (Examples 4, 5, and 6 of a comparison) The dispersant of an example 1 was replaced with the Nonion system surfactant (noy gene EAmade from Dai-Ichi Kogyo Seiyaku Co., Ltd. - 170), the anion system surfactant (high tenor by Dai-Ichi Kogyo Seiyaku Co., Ltd. - NO8), or the cation system surfactant (ASETAMIN-86 by Kao Corp.), respectively, the approach of an example 1 was repeated, and three sorts of ink was prepared. It admitted that condensation of a pigment begins to progress into an after [preparation] short time, and detailed-on actual distribution was not completed.

[0032] (Example 2) The dispersion medium in an example 1 was changed to the tetraethylene glycol monobutyl ether, and the approach of an example 1 was repeated. The same result as an example 1 was obtained except a marginal printing frequency being 8000Hz.

[0033] (Example 7 of a comparison) The dispersion medium of an example 2 was changed to the tetraethylene glycol monoethyl ether, the approach of an example 2 was repeated, and preparation and a printing trial of ink were performed. Although the same detailed distribution as an example 2 was possible, in the printing trial of the ink immediately after preparation, injection of ink stopped with ten nozzles between printings for 10 minutes with the printing frequency of 2000Hz. In the printing trial after a preservation stability test, injection of ink stopped with 15 nozzles between printings for 3 minutes with the printing frequency of 1000Hz at the time of heat. Also in the printing trial after the ordinary temperature preservation stability test of ink, it was the same dissatisfied result.

[0034] DBP oil absorption as a pigment 100 (ml / 100g), (Example 3) As the furnace carbon black (C.I.No.77266: Mitsubishi Chemical make MA-100) 9.0 section whose pH is 3.5, and a dispersant, C18 hydroxy-acid polyester 80Wt%, The ink which consists of the 9.0 sections of the admixture which consists of said stearyl alcohol sulfate Na salt 10Wt%, and the dipropylene glycol monobutyl ether 82.0 section which is a dispersion medium was prepared octadecanamide hydrochloride 10Wt% of the surfactant which is the assistant. In addition, it is in the middle of preparation of ink, and the 0.05 sections of a titanium coupling agent were added with the little volatile solvent. More than 99.4Wt% of a pigment particle was 1.0 micrometers or less in 0.03-micrometer or more particle size in ink, and mean particle diameter was 0.06 micrometers. In 20 degrees C, at 65cps and 60 degrees C, viscosity was 15cps and surface tension was 35 (mN/m). Without a marginal printing frequency's being 6000Hz and confusing a printing image by the contact in an after [printing] short time on each field for printing in a printing trial, the blot twisted, it was stable and high-speed printing was completed. Although injection of ink stopped with three nozzles after [of an after / printing initiation] 5 - 8 minutes when the printing frequency was set to 7000Hz, an injection halt of ink new after that did not take place. The good result with the same said [the printing trial after a preservation stability test and a heat cycle stability test] of the resumption trial of printing interruption was obtained at the time of the ordinary temperature preservation stability test of ink, or heat.

[0035] (Example 8 of a comparison) The dispersion medium of an example 3 was changed to dipropylene glycol monomethyl ether, and the approach of an example 3 was repeated. More than 99.5Wt% of a pigment particle was 1.0 micrometers or less in 0.02-micrometer or more particle size in ink, and mean particle diameter was 0.06 micrometers. In 20 degrees C, at 70cps and 60 degrees C, viscosity was 20cps and surface tension was 34 (mN/m). Although change was accepted in detailed distribution of a pigment neither

by the preservation stability test nor the heat cycle stability test at the time of the heat of ink, in the printing trial of the ink after preparation, injection of ink stopped even the printing frequency of 2000Hz with 15 nozzles between printings for 10 minutes.

[0036] (Example 4) The ink which consists of the silicon resin (X[by Shin-Etsu Chemical Co., Ltd.]-22-3939A) 8.0 section in which DBP oil absorption denaturalized by 90 (ml / 100g), and pH denaturalized by the amino group and the polyether radical as a pigment as the channel carbon black (C.I.No.77266: Degussa AG special black 4A) 7.0 section of 3.0 and a dispersant, and the diethylene-glycol monobutyl ether 85.0 section which is a dispersion medium was prepared. More than 99.3Wt% of a pigment particle was 1.0 micrometers or less in 0.03-micrometer or more particle size in ink, and mean particle diameter was 0.08 micrometers. In 20 degrees C, at 13cps and 60 degrees C, viscosity was 6cps and surface tension was 31 (mN/m). Without a marginal printing frequency's being 6000Hz and confusing a printing image by the contact in an after [printing] short time on each field for printing in a printing trial, the blot twisted, it was stable and high-speed printing was completed. The good result with the same said also of the printing trial after a preservation stability test or a heat cycle stability test or the resumption trial of printing interruption was obtained at the time of the ordinary temperature of ink, and heat.

[0037] (Example 9 of a comparison) The dispersion medium in an example 4 was changed to diethylene-glycol monobutyl ETERUMONO acetate, and the approach of an example 4 was repeated. Although the ink of detailed distribution could be prepared like the case of an example 4 and change was accepted in detailed distribution of a pigment neither by the preservation stability test nor the heat cycle stability test at the time of the ordinary temperature of ink, and heat, in the printing trial of the ink after preparation, injection of ink stopped even the printing frequency of 1000Hz with 18 nozzles between printings for 10 minutes.

[0038]

[Effect of the Invention] This invention is selection combination ***** about a resin system compound effective in these in specific glycol ether considering a specific carbon black pigment as a dispersion-medium object as a coloring agent. A pigment distributes as a detailed particle, the slit inside an ink jet printer is passed easily, and a particle does not condense by long-term neglect or preservation, And without spreading after printing, it was able to solidify in a short time and the solvent system black pigment ink for ink jet printers which can print high-speed was able to be offered to the field for permeability.

TECHNICAL FIELD

[The technical field to which invention belongs] This invention relates to the solvent system pigment ink at the time of printing with an ink jet printer to permeability ingredient sides, such as paper and timber.

PRIOR ART

[Description of the Prior Art] The printing technique of an ink jet print method is developed in recent years, and, generally it began to be used widely. Although various methods were proposed and the utilization phase is reached, it is common in them to inject at high speed and to make an image from ink to an object side, forming a detailed liquid ink drop. Since it is made to dissolve in various media and deals in a color as a coloring agent of ink, it is suitable for injecting forming a drop detailed as ink in a uniform dissolution condition. However, a color has a difficulty in lightfastness or a water resisting property, and the aspect of affairs of an activity has constraint. On the other hand, since the pigment is excellent in lightfastness or a water resisting property, it is desirable, but since there is no medium which dissolves it, it must be used as dispersion liquid of a very fine particle. It is the indispensable conditions for pigment ink that the supply way of the ink which

results in the nozzle and nozzle of a printer head from the demand of a print quality is detailed, and the particle diameter of the pigment which passes through that is still more detailed, and that must not condense at the time of an activity and storage, must not sediment, namely, a detailed distributed condition is maintained at stability. Although practical use is presented with pigment ink in some fields, since stable detailed distribution of a pigment which bears the severe condition of an ink jet print is difficult, the pigment ink in the field concerned is not yet put in practical use. The fate which becomes severer has a demand in the more minute ink [in / a high speed or if printing of a large area is called for more at all / more / an ink jet print] of endurance more like other print processes.

[0003] Although pigment ink for ink jet printers is desired for such a background, since the lightfastness of a pigment and a water resisting property have desiccation of ink or the slow solidification rate, and the printing image immediately after printing is confused by contact or they have many cases where the device for distribution becomes an enmity and the water resisting property of a print is inferior, in drainage system distribution of a satisfactory good thing, the pigment-content powder in a non-drainage system is desirable. Moreover, among nonaqueous dispersion media, although a volatile solvent can expect desiccation solidification of the prompt ink by evaporation of the solvent after printing, it takes place [change of the presentation by volatilization / tend] at the times of handling, such as the time of printing, and is unsuitable. If the interior of paper or the woody field for permeability is permeated promptly and ink solidifies with the solvent of comparatively difficulty volatility at the time of printing, a pigment will be spread on an object side front face, a printing image will spread by contact, or it will not be confused, and it will be assumed that minute printing is possible. It seems to be whether ink permeates the detailed part of a print head well, and this can supply ink certainly, and a problem of the same kind. It seems that however, there is no knowledge what kind of dispersion medium can respond to high-speed printing more by combining stable detailed distribution and such a good osmosis fluidity in relation by the pigment or the dispersant.

EFFECT OF THE INVENTION

[Effect of the Invention] This invention is selection combination ***** about a resin system compound effective in these in specific glycol ether considering a specific carbon black pigment as a dispersion-medium object as a coloring agent. A pigment distributes as a detailed particle, the slit inside an ink jet printer is passed easily, and a particle does not condense by long-term neglect or preservation, And without spreading after printing, it was able to solidify in a short time and the solvent system black pigment ink for ink jet printers which can print high-speed was able to be offered to the field for permeability.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Development of the pigment ink for ink jet printers which carried out detailed distribution of the pigment at the dispersion medium of a non-drainage system which secures both the osmosis fluidities of detailed stable distribution of a pigment, and ink.

MEANS

[Means for Solving the Problem] The object achievement is expected by selection of a new ink presentation or a compounding ratio.

[0006] Since the ink jet print method optimal as an object is a piezo method which performs the formation of a

detailed drop and injection of ink by the piezo-electric element when aiming at development of the pigment ink for ink jet printers which carried out detailed distribution of the pigment to the dispersion medium of a non-drainage system, the method will be made into an example and the content of this invention will be stated more to a detail. By the piezo method, electric oscillation is changed into a dynamics oscillation, it tells ink, ink is turned to an object side from two or more holes with a detailed nozzle, and it injects as a detailed drop. Injection of a detailed drop is controlled by the electric-oscillation input to a piezo-electric element, controls the attainment location of the ink on an object side by migration of an object side or a printer nozzle, and draws a desired image. A piezo-electric element is arranged in dozens of micrometer or more location to which it is about hundreds of micrometers and opening of some holes is usually expected in the medium, and, as for the path of the supply way of the ink in which the diameter of opening of the hole of a nozzle usually reaches dozens of micrometers and there, dozens of components are usually arranged from some with the whole nozzle. Since opening and the passage of the neighborhood of it are detailed, naturally stable detailed distribution of a pigment becomes an indispensable condition.

[0007] Although a certain amount of guess was possible, and the ink there is no change in the viscosity of the detailed distributed condition of a pigment or ink, and it is considered that is stability was prepared when actually saved under heating or a heat cycle when it was the simple problem into what kind of combination a pigment, a dispersion medium, and a dispersant should have been made in pigment ink other than for ink jet printers, the ink which was able to be printed favorably at the beginning of printing test initiation stops [injection of ink] after a while. That is, the scale taken in development of conventional various ink is not helpful. When printing of long duration was not completed in a practical print speed although the continuity of injection of ink with the device of a dispersant improved to some extent when the solvent with the high hydrophilic property which has water and compatibility, for example according to other examination of this invention persons was made into the dispersion medium, and the hydrophobic, strong solvent was made into the dispersion medium, even if it devised various dispersants, injection of ink was unsuitable like the above-mentioned. That is, with neither the single scale of a hydrophilic property or hydrophobicity, nor the single scale of a dispersant, solution is in prospect. If it says whether ink is equal also to the high-speed oscillation of thousands of Hz of the piezo-electric element at the time of printing, and detailed passage may be flowed through to stability, and whether many demands which are described below can also be filled simultaneously, in well-known knowledge, the guide of solution will not be acquired conventionally.

[0008] The ink the quantity of was decreased by injection is supplied from an ink reservoir of the supply way other end by the capillarity in the supply way which is a capillary. The surface tension and the viscosity property of ink must be chosen for supplying the ink to the head of a nozzle smoothly. Although it is generally so advantageous to capillarity that surface tension is large, when first filled up with ink, air bubbles are generated in passage or it is easy to remain in it, and while it prints, it is possible [it] to blockade passage. Once it does not ask whether it is based on a condensation pigment, or it is based on air bubbles but blockades, since injection of ink becomes impossible, if the nozzle stops printing and passage of ink is not reashed, it cannot be used any longer. An injection halt took place in many cases, degassing was not able to be beforehand carried out by supersonic vibration, and a solvent independent examined the surfactant as a dispersant of ink, and each-other gap has not improved it, either. When the viscosity of ink is too high, its drift velocity is slow, high-speed floating in the capillary corresponding to the injection performed at high speed is impossible, supply of ink cannot be followed, if too low, overflow will be carried out from a nozzle, the ink of a printing image will be superfluous and it will be confused. Moreover, before the argument of the absolute value of viscosity, if viscous behavior is not a Newtonian flow, inconvenience will arise. Surface tension and a viscosity property are also likely to influence thin drop-ization of the injected ink, and are likely to have the range suitable for forming the drop of proper magnitude, in view of the printing image. However, it is specifically unknown.

[0009] Two or more drops of the injected ink form the printing image of the line breadth beyond it from a submillimeter meter on an object side at the time of cm. Line breadth and its intermittence length are

controlled by actuation of a piezo-electric element. Since the object sides of printing are paper and a woody permeability side, a dispersion medium needs to be the matter which leaves a pigment to a front face, permeates the interior of a field promptly, and, and a printing image does not spread by contact or is not carried out. [that a pigment is spread on the front face of an object side] Although it is whether ink permeates the detailed part of a print head well, and this can supply ink certainly, and a problem of the same kind, since the nature of a cellulose or others, or a composite organic macromolecule and the composite inorganic quality of packing are contained and it is constituted, the field for printing is not identically discussed to a head being metal.

[0010] As for a loan, the hand of presentation combination which fills many various demands as mentioned above simultaneously is not obtained easily. When oleyl alcohol was chosen as an organic dispersion-medium object as a result of many trial-and-error, this invention person found out that the solvent system pigment ink for ink jet printers could be constituted using various pigments, and already applied as Japanese Patent Application No. 11-209022. However, according to a subsequent examination, although applied ink was excellent in distributed stability or a printing property, it became clear that practically still more advanced distributed stability should have been provided. For this reason, this invention persons continued amelioration research and reached this invention about black ink.

[0011] In the ink presentation of this invention, DBP oil absorption is below or more 15 180 (ml / 100g), and the pigment which is a coloring agent is carbon black which pH presents the acidity within the limits of 4.5 or less [2.0 or more]. Although it was possible, even if the detailed distribution with titanium oxide and the inorganic pigment like red ocher stable in standing or a comparatively quiet floating scene put various creativity on the object of this invention, lock out of printing passage happens and was unsuitable [distribution]. Also although it is called a carbon black pigment, DBP oil absorption is a thing within the limits below or more 15 180 (ml / 100g). And the carbon black which pH presents the acidity within the limits of 4.5 or less [2.0 or more] is used. More than 98.0Wt% of a pigment particle is 1.0 micrometers or less in 0.01-micrometer or more particle size in ink. Mean particle diameter was within the limits of 0.02 micrometers or more 0.5 micrometers or less, when distributing to stability in the specific organic medium containing the effective below-mentioned dispersant, lock out of printing passage did not take place, but clear printing was possible. If lock out of printing passage becomes easy to take place the device of lowering of the pigment loadings at the sacrifice of buildup of dispersant loadings, or lowering of printing concentration when oil absorption deviates from the above-mentioned range etc. as drawing and particle size and pH deviate from the above-mentioned range, in the case where printing clear in lock out of printing passage taking place becomes impossible, it increases and is unsuitable. Moreover, if such conditions are not fulfilled, reservation of the detailed stability at the time of the long-term storage of ink is inadequate, and difficulty is in an activity. In addition, DBP oil absorption and pH are the parameters in connection with the description of a well-known particulate matter in this industry, for example, pH is a value measured according to JIS-K6221. Oil absorption is below or more 20 160 (ml / 100g), and the range especially desirable from the above viewpoints is the case where more than 99.0Wt% of a pigment particle is 0.8 micrometers or less in 0.03-micrometer or more particle size in ink, mean particle diameter is within the limits of 0.04 micrometers or more 0.5 micrometers or less using the carbon black which pH presents the acidity within the limits of 4.0 or less [2.5 or more], and it is distributing to stability.

[0012] Carbon black can be carried out in the ink of this invention, without asking any of channel black or furnace black it is, if the conditions of point ** are fulfilled. Moreover, it is possible to use together one sort or two sorts or more for comparatively a small amount of organic pigment to carbon black for the object, such as adjustment of a delicate color tone. It is possible to be the range which does not spoil any properties other than the color tone of ink jet ink, and to choose and use the class and amount together as a pigment which can be carried out by this invention, from pigments, such as azo pigment, condensation azo pigment, phthalocyanine pigment, an anthraquinone system pigment, a perylene pigment, a peri non pigment, a quinacridone pigment, and a dioxazine pigment.

[0013] The dispersion mediums in the ink presentation of this invention are one sort chosen from the group

which the degree of polymerization of an ethyleneoxide chain or a propylene oxide chain becomes from the monobutyl ether of or more 2 four or less polyethylene glycol, or the monobutyl ether of propylene glycol, or those two sorts or more of mixture. That is, they are one sort chosen from the group which consists of the diethylene-glycol monobutyl ether, the triethylene glycol monobutyl ether, the tetraethylene glycol monobutyl ether, the dipropylene glycol monobutyl ether, the tripropylene glycol monobutyl ether, and the tetrapropylene glycol monobutyl ether, or those two sorts or more of mixture. When a pigment is carbon black of point **, the object of this invention is reached by this dispersion-medium object combining and being used with the below-mentioned resin system dispersant.

[0014] Even if it tried the activity by making the saturation fatty alcohol of the shape of a straight chain, and the letter of branching into a dispersion medium, lock out of printing passage took place, injection of ink stopped, and continuous printing was impossible. Since the straight chain-like saturation fatty alcohol with a carbon number big especially was crystallized in ordinary temperature, even if it maintained passage at the bottom of heating, lock out of printing passage took place. However, although oleyl alcohol was exceptionally [in alcohols] promising, lock out of ink passage took place in long-term printing accompanied by injection division interruption of long duration. Although the various solvents known as unsaturated fatty acid, such as oleic acid, the ester of those or glycol ether other than the monobutyl ether of the specific polyalkylene glycol comparatively specified to the polyalkylene glycol and this invention of low molecular weight, and other dispersion media of pigment ink were examined changing the class of pigment, the distributed approach, and the class and the blending ratio of coal of a dispersant that are used together, the object useful as a medium in which stable long-term printing is possible was not able to be found out. In the ink kept under standing or a comparatively moderate oscillation, though it was ink of stable detailed distribution, when the printing trial was presented, an injection halt of ink took place.

[0015] If that situation is described now somewhat in detail, the injection quantity of the ink from the nozzle which has a printer head with the printing passage of time begins to fall, moreover, the injection from that nozzle will stop after a while, an injection way will carry out sequential generating also with turbulence and the nozzle of the others [phenomenon / this] on the same head, and the number of nozzles of an injection halt will be expanded. If such a phenomenon happens, printing is already impossible. An injection halt of one nozzle must not take place over long duration practically, either. Printing cannot be resumed, if the vibration frequency of a piezo-electric element is reduced, it becomes same situation and overhaul cleaning of a head is not performed, although time amount until an injection halt of the ink after printing test initiation takes place is prolonged. Since the part which runs short of the injection quantity of the ink at the time of printing, and a print speed will fall although time amount until an injection halt takes place is prolonged further if the vibration frequency of a piezo-electric element is reduced further, the practical value as [both] ink falls. The decisive cause is unknown although the guess that an injection halt will be what is depended on condensation of a pigment, or mixing or generating of air bubbles in the detailed passage of a printer head is possible. It also became clear that, as for the ink in which an injection halt takes place with the printing passage of time, an injection halt comes to take place into a short time by the prolonged storage back. Moreover, it became clear that it was in case ink will not blockade and inject it, either, if the ink in which a series of favorable printings to which an injection halt does not take place are possible is also left setting ink in an ink jet printer after ending printing, goes through a certain time amount and resumes printing.

[0016] According to examination of this invention persons, only when the degree of polymerization of an ethyleneoxide chain or a propylene oxide chain moreover chose the selection combination of a pigment and a dispersion medium like this invention through the monobutyl ether of or more 2 four or less polyethylene glycol, the monobutyl ether of propylene glycol, or those mixture, continuation and intermittent printing of a long period of time [ink / after preparation or prolonged storage] were possible. This assessment approach and an assessment result are explained in full detail after the paragraph number 0026.

[0017] Since other descriptions which the dispersion medium of this invention has permeate the interior of an object side promptly, making diffusion osmosis of a pigment into the minimum, namely, making a blot of a

printing image into the minimum, and leaving many of pigment particles on a front face moreover after a liquid ink drop arrives at the field for printing, they are that turbulence of a printing image does not take place even if a printing image can form vividly deeply and it contacts in an after [printing] short time. The pigment solidification (on these descriptions, this may also be indicated to be "desiccation") by osmosis into the printing side of a medium which is not desiccation solidification of the ink by evaporation of a medium takes place promptly. a kind of suitable chromatography for this printing – graphic effectiveness was unexpected discovery. Although this effectiveness was boiled to that extent with the construction material and structure of an object side, the class and description of the pigment used, a class, a compounding ratio of a dispersant, etc. and that difference had it a little, its selection of a dispersion medium was decisive. By the other type dispersion medium, even if it was glycol ether, for example, when the molecular weight was smaller than the specific glycol ether of this invention, although desiccation was quick, stable injection was not completed, because the viscosity of ink was high when molecular weight was large, stable injection was not completed, and many cases where a blot and desiccation were dissatisfied were accepted at the ring content medium, for example, bis-alkyl phthalate, and it was unsuitable. As compared with the difference in the long-term distribution stability in that the monobutyl ether glycol which is a dispersion-medium object in this invention is independent, or the case of using an other type medium, although it can carry out with those mixture and the difference in volatility or permeability is among them, the difference does not become a problem small.

[0018] The dispersant in the ink presentation of this invention should just be the safe matter which may distribute [a dispersion medium] the pigment of point ** to stability minutely. As a dispersant for generally distributing a pigment in a medium, although many matter is proposed, if the combination of a pigment and a dispersion medium is limited, there are few effective dispersants unexpectedly and, moreover, the class of effective dispersant changes with combination of a pigment and a dispersion medium. however, the engineer of the field concerned – an effort – **** trap ***** – the selection by experiment of an effective dispersant is possible. According to examination of this invention persons, the matter which may distribute a pigment to stability minutely in the pigment of this invention and the combination of a dispersion medium with various kinds of matter classified also as a surfactant was not able to be found out.

[0019] On the other hand, there is nothing or it became clear that the matter which is a surface activity operation and which suits the object of this invention was in few resin system compounds. That is, an ethyleneoxide-propylene oxide copolymer, aliphatic series polyester, the aliphatic series polyester that denaturalized of the amine component, the silicon resin which denaturalized of the amine component or the polyether component, a polyvinyl butyral, various acrylic copolymers, etc. were effective in stable detailed distribution. The matter which is not effective also exists plentifully like ethyl cellulose etc. also in the matter said for there to be a distributed operation generally on the other hand. And there is also matter which uses as ink for ink jet printers, and becomes only hot ink also in the effective dispersant since the viscosity of ink will become high like a polyvinyl butyral if it is not a low-molecular-weight article comparatively. The ink which suits the object of this invention in an ethyleneoxide-propylene oxide copolymer, aliphatic series polyester, the aliphatic series polyester that denaturalized of the amine component, and the silicon resin which denaturalized of the amine component or the polyether component was possible. Although the dispersant which can be carried out by this invention besides the compound illustrated above may exist, it should just use the possible dispersant of clear printing which observes saving under standing or a comparatively loose oscillation, can secure stable detailed distribution, moreover continues on the ink jet print of a piezo method, and does not have a blot, choosing it. In addition, concomitant use of a small amount of distributed assistant for demonstrating more highly the effectiveness of the dispersant performed by the technical field concerned being sufficient is possible also in this invention. As a distributed assistant, various kinds of surfactants, the organic base nature matter, etc. can be raised as the example, can select an effective thing and its amount suitably according to the class of pigment used, and can use together as some dispersants. Moreover, in concomitant use of a distributed assistant, using comparatively a small amount of diluent for the facilities of measuring or handling can be carried out, unless the property of the ink of this invention is spoiled. The

dispersant which similarly are the objects for chemical stability reservation of a dispersant etc., and contains the little additive for dispersant resin can also be carried out unless the property of the ink of this invention is spoiled.

[0020] In the solvent system black pigment ink for ink jet printers of this invention which uses a coloring agent, an organic dispersion-medium object, and a dispersant as an indispensable component, less than [of the pigment with which a dispersant uses / per indispensable component 100 weight section of ink and a pigment / the compounding ratio of an indispensable component below the 15.0 weight sections more than the 1.0 weight section / more than 0.1 weight twice 2.0 weight twice], and the remainder are dispersion mediums. It causes [if / than the above-mentioned value / too little / a pigment compounding ratio /, the coloring concentration of ink is clearly inadequate and become scarce at practicability, if excessive, the fluidity of ink gets worse, and / the fluidity within a printer head] trouble especially and is unsuitable although it changes with classes of pigment. although it changes a little with classes of dispersant, if it is hard to secure detailed and stable distribution of a pigment clearly if [than the above-mentioned value] too little [the compounding ratio of a dispersant] and excessive – already – buildup of the contribution to pigment-content powder – or moreover the viscosity of ink becomes high, and trouble is caused to the fluidity within a printer head, and the rate of drying in the field for printing of ink becomes late and is unsuitable. It is the case where less than [of the pigment with which a dispersant uses / per indispensable component 100 weight section of ink and a pigment / a more suitable compounding ratio below the 12.0 weight sections more than the 5.0 weight sections from the above viewpoint / more than 0.2 weight twice 1.5 weight twice], and the remainder are dispersion media. The ink of this invention is the constituent which added the little additive component of point ** or the after-mentioned to combination of the above-mentioned indispensable component if needed.

[0021] In the solvent system pigment ink for ink jet printers of this invention, the ink which consists only of an indispensable component is hypoviscosity dispersion liquid of the Newton fluidity. Although the viscosity of ink changes with classes, compounding ratios, etc. of a pigment or a dispersant, it is 1-20cps at 10-100cps and 60 degrees C in 20 degrees C generally. Since detailed and stable distribution of a pigment is secured, viscosity is also stable with time. And since change by viscous temperature is small, there is little fluctuation of the injection condition of the ink by environmental temperature change of a print head. On the contrary, it is possible to present an activity in the temperature requirement which heats the ink passage of a print head and its near in order to lose fluctuation of a delicate injection tune, and results in 100 degrees C beyond ordinary temperature, and it is desirable to present an activity in the condition of having been especially maintained at a certain constant temperature in the temperature requirement concerned.

[0022] It comes to be below an outline when the manufacture approach of the ink of this invention is illustrated. A pigment, a dispersant, and the specified quantity of a dispersion medium are measured, and after carrying out stirring mixing, in the disperser of common knowledge in the fields concerned, such as a bead mill and 3 roll mills, grinding and micro-disperse-izing of a pigment are performed and it considers as ink. The pigments of a start raw material are fine particles which consist of an aggregated particle which many of a primary particle usually condensed, and they are distributed in a dispersion medium while they grind an aggregated particle with wet as mentioned above and make this a more detailed particle. since grinding and micro-disperse-ization are performed simultaneously – only – a distributed process – it has called distributing. It is possible to make into a desired value the pigment particle diameter distributed by changing the conditions of a distributed process and its distribution. Since it distributes more effectively, the remaining dispersion medium is added to the thick dispersion liquid which distributed using a dispersion medium fewer than the specified quantity, and were obtained, distribution is completed, the approach often performed also considers as the ink of a desired presentation ratio, and it can be carried out also in this invention. When there is a big and rough particle of grinding imperfection with a minute amount in a distributed process When correcting to eye the low one a little the viscosity of the ink which removed this by approaches, such as centrifugal separation, or has been manufactured normally for the specific object Add a dispersion medium, add, the solvent, i.e., the viscosity accommodation solvent, of a dispersion medium and compatibility which moreover

does not have an adverse effect on distribution, or The distributed assistant of point ** can be used together, or qualification of adding a defoaming agent suitable when addition of a defoaming agent is desirable can be suitably carried out in the appropriate phase of ink manufacture of this invention according to manufacture or the service condition of ink.

[0023] In the ink of this invention, although a solvent usable as a viscosity modifier is reached at a variety if needed, fatty acid ester, such as glycol ether, such as glycols [, such as triethylene glycol and tripropylene GURIKORURU], methyl - or ethylcellosolve, and methyl - or ethyl carbitol, a tree, or the monopropyl ether of tetraethylene glycol, oleic acid octyl, and sorbitan monolaurate, is mentioned as the example. extent with which, as for the addition, change of printing properties other than the viscosity of ink is permitted – it should stop – the indispensable component of ink – at most – it is less than [20Wt%]. When it desires hypoviscosity-ization more, it is good to correct high the compounding ratio of the dispersion medium of the indispensable component of ink, and to prepare new ink. In the ink of this invention, the denaturation polysiloxane by the polysiloxane, copolymerization, etc. is illustrated as a defoaming agent which can be added if needed. The addition is or less about [of ink] 1Wt%, and is enough. Moreover, although a silane coupling agent and a titanium coupling agent may be added by ink in order to raise the fixing reinforcement of the ink to the field for printing, also in this invention, addition of a coupling agent is possible if needed, and an addition is or less about [of ink] 1Wt%, and is enough.

[0024] As stated above, this invention a specific carbon black pigment as a dispersion-medium object as a coloring agent by using specific glycol ether combining the effective resin system compound as a dispersant. A pigment distributes as a detailed particle, the slit inside an ink jet printer is passed easily, and a particle does not condense by long-term neglect or preservation, And it dries for a short time, without spreading after printing, and the solvent system pigment ink for ink jet printers which can print high-speed is offered. The ink of this invention fits the front face of papers, such as printing and an information form, a package form, a liner and corrugating medium, and the mounting paper, a white board, or the woody permeability ingredient currently widely called plywood and a plywood printing by the ink jet print method, especially the piezo method. All the things that can be printed with ink jet printers, such as graphic forms, such as various kinds of alphabetic characters, a figure, a bar code, and a logo mark, various kinds of patterns, and a poster, are possible for a printing image.

[0025] Hereafter, an example is given about this invention and it explains to a detail more. The section in the inside of an example is the weight section. In preparation of ink, the bead mill distributed using 2/5 amount of the dispersion medium of a schedule, and after taking out thick ink, in addition to the bottom of stirring, the remaining dispersion medium was used as the ink of a predetermined compounding ratio to serve also as concentration adjustment. The pigment particle diameter in ink was measured by the dynamic light scattering which performs frequency analysis of the laser-doppler effectiveness. The viscosity of ink was measured at 20 degrees C and 60 degrees C using the Brookfield viscometer. The surface tension of ink was measured at the room temperature with the WIRUHERUMI type surface tension balance.

[0026] After the diameter of opening of a blowout hole was led to 50 micrometers in one pipe and ink is led to a head using the print head by which the nozzle in which the ink jet print trial of ink has three ink blowout holes per piezo-electric element has been arranged at the 30-piece serial, it branches for 30 nozzles within a head, each leads to three ink blowout holes, and the path of the narrowest place of passage is 100 micrometers. a nozzle – 60-degree C constant temperature – it maintained at the condition. Sequential change of the oscillation frequency (henceforth a printing frequency) of the piezo-electric element for ink injection is carried out by 1000Hz unit from 1000Hz to 8000Hz. In this trial, it continues from all nozzles to stability at least 30 minutes or more, and asks for the printing frequency (marginal printing frequency) of the limitation which can inject ink favorably. in addition, although it can be regarded as the possible ink of printing even if a marginal printing frequency is less than [1000Hz or it] in this testing machine, the marginal printing frequency of 3000Hz or more is desirable, considering the trend of the society which sees and exceeds high-speed printing. It was left as a field for printing of permeability, without whether it is favorably injected by the line of constant

width, without printing moving this using a copy paper, the kraft paper in the corrugated fiberboard Hara paper, a white board, and plywood, and ink breaking off, whether a printing image is confused by the contact in an after [printing] short time again, and contacting, and extent of a blot of a printing image was observed visually. The ordinary temperature preservation stability test of the ink which performs the above-mentioned printing trial after saving ink for 30 days in the ordinary temperature in a release container in order to see the distributed stability of the pigment in ink, After saving ink for 14 days during a sealing container and a 80-degree C air bath, it returns to ordinary temperature. The heat cycle stability test of the ink which performs a printing trial after repeating 5 times, placing a preservation stability test and ink subsequently to under a -20-degree C air bath every 14 hours during a 80-degree C air bath for 12 hours at the time of the heat of the ink which performs the above-mentioned printing trial, After suspending printing for 24 hours, filling up a printing testing machine with ink, the resumption trial of printing interruption which resumes printing was carried out suitably.

EXAMPLE

[Example] (Example 1) 90 (ml / 100g) and pH prepared [DBP oil absorption] as a pigment the ethyleneoxide-propylene oxide block-copolymer 7.0 section and the ink in which it consists of the triethylene glycol monobutyl ether 84.8 section and the diethanolamine 0.2 section as a dispersion medium as the channel carbon black (C. special black by I.No.77266:Degussa AG 4A) 8.0 section of 3.0, and a dispersant. More than 99.5Wt% of a pigment particle was 1.0 micrometers or less in 0.01-micrometer or more particle size in ink, and mean particle diameter was 0.05 micrometers. In 20 degrees C, at 62cps and 60 degrees C, viscosity was 17cps and surface tension was 31 (mN/m). Without a marginal printing frequency's being 6000Hz and confusing a printing image by the contact in an after [printing] short time on each field for printing in a printing trial, the blot twisted, it was stable and high-speed printing was completed. The good result with the same said also of the printing trial after a preservation stability test and a heat cycle stability test and the resumption trial of printing interruption was obtained at the time of the ordinary temperature preservation stability test of ink, and heat.

[0028] (Example 1 of a comparison) The pigment of an example 1 was changed to the fumace carbon black (C.I.No.77266: VULCAN XC[by Cabot Corp.]-72R) whose DBP oil absorption is 178 (ml / 100g) and whose pH is 5.0, the approach of an example 1 was repeated, and preparation and a printing trial of ink were performed. More than 99.5Wt% of a pigment particle was 1.0 micrometers or less in 0.04-micrometer or more particle size in ink, and mean particle diameter was 0.08 micrometers. In 20 degrees C, at 35cps and 60 degrees C, viscosity was 15cps and surface tension was 31 (mN/m). Although change was not accepted in detailed distribution of a pigment by the preservation stability test or heat cycle stability test of ink before a printing trial, in the printing trial of the ink after preparation, injection of ink stopped even the printing frequency of 1000Hz with nine nozzles between printings for 15 minutes.

[0029] (Example 2 of a comparison) The pigment of an example 1 was changed to the fumace carbon black (C.I.No.77266: the Degussa AG pudding tex 90) whose DBP oil absorption is 95 (ml / 100g) and whose pH is 9.0, the approach of an example 1 was repeated, and preparation and a printing trial of ink were performed. Although the same detailed distribution as an example 1 was possible, the inclination of flocking settling was slightly accepted in distribution of a pigment by the preservation stability test or the heat cycle stability test at the time of the heat of the ink before a printing trial. In the printing trial of the ink immediately after preparation, injection of ink stopped with 13 nozzles between printings for 2 minutes with the printing frequency of 1000Hz. Also in the printing trial after the ordinary temperature preservation stability test of ink, it was the same dissatisfied result.

[0030] (Example 3 of a comparison) The dispersion medium of an example 1 was changed to the triethylene glycol monomethyl ether, the approach of an example 1 was repeated, and preparation and a printing trial of

ink were performed. Although the same detailed distribution as an example 1 was possible, in the printing trial of the ink immediately after preparation, injection of ink stopped with 15 nozzles between printings for 5 minutes with the printing frequency of 1000Hz. In the printing trial after a preservation stability test, injection of ink stopped with 13 nozzles between printings for 2 minutes with the printing frequency of 1000Hz at the time of heat.

[0031] (Examples 4, 5, and 6 of a comparison) The dispersant of an example 1 was replaced with the Nonion system surfactant (noy gene EAmade from Dai-Ichi Kogyo Seiyaku Co., Ltd. - 170), the anion system surfactant (high tenor by Dai-Ichi Kogyo Seiyaku Co., Ltd. - NO8), or the cation system surfactant (ASETAMIN -86 by Kao Corp.), respectively, the approach of an example 1 was repeated, and three sorts of ink was prepared. It admitted that condensation of a pigment begins to progress into an after [preparation] short time, and detailed-on actual distribution was not completed.

[0032] (Example 2) The dispersion medium in an example 1 was changed to the tetraethylene glycol monobutyl ether, and the approach of an example 1 was repeated. The same result as an example 1 was obtained except a marginal printing frequency being 8000Hz.

[0033] (Example 7 of a comparison) The dispersion medium of an example 2 was changed to the tetraethylene glycol monoethyl ether, the approach of an example 2 was repeated, and preparation and a printing trial of ink were performed. Although the same detailed distribution as an example 2 was possible, in the printing trial of the ink immediately after preparation, injection of ink stopped with ten nozzles between printings for 10 minutes with the printing frequency of 2000Hz. In the printing trial after a preservation stability test, injection of ink stopped with 15 nozzles between printings for 3 minutes with the printing frequency of 1000Hz at the time of heat. Also in the printing trial after the ordinary temperature preservation stability test of ink, it was the same dissatisfied result.

[0034] DBP oil absorption as a pigment 100 (ml / 100g), (Example 3) As the furnace carbon black (C.I.No.77266: Mitsubishi Chemical make MA-100) 9.0 section whose pH is 3.5, and a dispersant, C18 hydroxy-acid polyester 80Wt%, The ink which consists of the 9.0 sections of the admixture which consists of said stearyl alcohol sulfate Na salt 10Wt%, and the dipropylene glycol monobutyl ether 82.0 section which is a dispersion medium was prepared octadecanamide hydrochloride 10Wt% of the surfactant which is the assistant. In addition, it is in the middle of preparation of ink, and the 0.05 sections of a titanium coupling agent were added with the little volatile solvent. More than 99.4Wt% of a pigment particle was 1.0 micrometers or less in 0.03-micrometer or more particle size in ink, and mean particle diameter was 0.06 micrometers. In 20 degrees C, at 65cps and 60 degrees C, viscosity was 15cps and surface tension was 35 (mN/m). Without a marginal printing frequency's being 6000Hz and confusing a printing image by the contact in an after [printing] short time on each field for printing in a printing trial, the blot twisted, it was stable and high-speed printing was completed. Although injection of ink stopped with three nozzles after [of an after / printing initiation] 5 - 8 minutes when the printing frequency was set to 7000Hz, an injection halt of ink new after that did not take place. The good result with the same said [the printing trial after a preservation stability test and a heat cycle stability test] of the resumption trial of printing interruption was obtained at the time of the ordinary temperature preservation stability test of ink, or heat.

[0035] (Example 8 of a comparison) The dispersion medium of an example 3 was changed to dipropylene glycol monomethyl ether, and the approach of an example 3 was repeated. More than 99.5Wt% of a pigment particle was 1.0 micrometers or less in 0.02-micrometer or more particle size in ink, and mean particle diameter was 0.06 micrometers. In 20 degrees C, at 70cps and 60 degrees C, viscosity was 20cps and surface tension was 34 (mN/m). Although change was accepted in detailed distribution of a pigment neither by the preservation stability test nor the heat cycle stability test at the time of the heat of ink, in the printing trial of the ink after preparation, injection of ink stopped even the printing frequency of 2000Hz with 15 nozzles between printings for 10 minutes.

[0036] (Example 4) The ink which consists of the silicon resin (X[by Shin-Etsu Chemical Co., Ltd.]-22-3939A) 8.0 section in which DBP oil absorption denaturalized by 90 (ml / 100g), and pH

denaturalized by the amino group and the polyether radical as a pigment as the channel carbon black (C.I.No.77266: Degussa AG special black 4A) 7.0 section of 3.0 and a dispersant, and the diethylene-glycol monobutyl ether 85.0 section which is a dispersion medium was prepared. More than 99.3Wt% of a pigment particle was 1.0 micrometers or less in 0.03-micrometer or more particle size in ink, and mean particle diameter was 0.08 micrometers. In 20 degrees C, at 13cps and 60 degrees C, viscosity was 6cps and surface tension was 31 (mN/m). Without a marginal printing frequency's being 6000Hz and confusing a printing image by the contact in an after [printing] short time on each field for printing in a printing trial, the blot twisted, it was stable and high-speed printing was completed. The good result with the same said also of the printing trial after a preservation stability test or a heat cycle stability test or the resumption trial of printing interruption was obtained at the time of the ordinary temperature of ink, and heat.

[0037] (Example 9 of a comparison) The dispersion medium in an example 4 was changed to diethylene-glycol monobutyl ETERUMONO acetate, and the approach of an example 4 was repeated. Although the ink of detailed distribution could be prepared like the case of an example 4 and change was accepted in detailed distribution of a pigment neither by the preservation stability test nor the heat cycle stability test at the time of the ordinary temperature of ink, and heat, in the printing trial of the ink after preparation, injection of ink stopped even the printing frequency of 1000Hz with 18 nozzles between printings for 10 minutes.
